A HISTORY

OF

CHEMICAL THEORIES
AND LAWS

BY

M. M. PATTISON MUIR, M.A.

Fellow and Prælector in Chemistry of Gonville and Caius College, Cambridge

"The great object, in trying to understand history, political, religious, literary, or scientific, is to get behind men, and to grasp ideas."
<div align="right">LORD ACTON'S LETTERS.</div>

"Dans l'étude de la nature, comme dans la pratique de l'art, il n'est pas donné à l'homme d'arriver au but sans laisser des traces des fausses routes qu'il a tenues."
GUYTON DE MORVEAU, in *Encyclopédie Méthodique (1786)*.

𝔗o the 𝔐emory of

THE MASTER

ANTOINE LAURENT LAVOISIER

I dedicate this history of parts of the science which it was his glory to form from the materials gathered by himself and by many who went before him during more than two thousand years.

PREFACE.

THE more I try to understand chemistry, the more I am convinced that the methods, achievements, and aims of the science can be realized only by him who has followed the gradual development of chemical ideas. A just judgment can be passed on the relative importance of the methods which are used, the results which are obtained, and the problems which are being attacked by the chemists of to-day, only when a careful study has been made of the methods employed, the results gained, and the points of attack selected by the chemists of the past.

I have not attempted the uncalled for task of writing a history of chemistry. To do that, at present, would be to produce a mighty volume, containing a series of text-books, a bewildering catalogue of facts, and a sheaf of biographical essays, supplemented by prolegomena, appendices, and chronological tables.

The object of this book is to set forth what seem to me the main lines along which the science of chemistry has advanced to its present position. In making an attempt to do this, in an orderly fashion, with some fulness of detail, and, I hope, some sense of proportion, I have passed over very many able memoirs; I have not mentioned the chemical histories of particular substances, except in so far as these have appeared to me to illustrate the development of some law, theory, or hypothesis of general importance. I describe only those investigations which, in my judgment, have given powerful impulses to the advance of chemical science along paths already trodden, or

have opened new ways of progress. Of course, I do not pretend to describe every investigation which can legitimately claim to come under these categories.

By confining myself to the greater chemical movements, to the seminal work in chemical science, I am saved from those petty controversies about priority which are valueless when one is trying "to get behind men, and to grasp ideas."

To trace the development of chemical ideas without referring, in considerable detail, to the progress of physical chemistry, would be impossible; but, because of inclination, and also because of personal limitations, I have not wandered far from the main roads of *chemical* science.

Some may say I have omitted much that is important, others may think I have included not a little that is trivial. In such matters a writer must use his own judgment, after he has trained it to the best of his ability.

I have verified all my references, and read with care every memoir, pamphlet, and book whereof I give more than a passing notice.

<div align="right">M. M. Pattison Muir.</div>

Cambridge, Eng.
   June, 1906.

INTRODUCTION.

ARRANGEMENT OF SUBJECT-MATTER.

THE purpose of chemistry seems to have changed much from time to time. At one time chemistry might have been called a theory of life, and at another time a department of metallurgy; at one time a study of combustion, and at another time an aid to medicine, at one time an attempt to define a single word, the word *element*, and at another time the quest of the unchanging basis of all phenomena. Chemistry has appeared to be sometimes a handicraft, sometimes a philosophy, sometimes a mystery, and sometimes a science.

A chronological treatment of the history of chemistry must give the impression that the drift of the science at certain times was quite unlike that at other periods. It would not be very difficult, I suppose, to make a summary of the prominent features of each period of chemical advance in a descriptive formula; but the more completely that were done, the more unreal would be the result. As the purpose of this book is to show how the main conceptions of chemistry have arisen, widened, strengthened, gained or lost ground, this purpose will be better served by taking changes in the general ideas of the science as the landmarks than by arranging the history of the subject in chronological periods.

It may be said that to trace the development of each general principle of chemistry demands a selection and an arrangement of the material such that the result is rather a considera-

tion of the growth of the science from an outside position than an attempt to live through each period along with those who made the advances in that period. I admit this objection to the method I intend to follow; and I also admit that the method cannot be pursued without repeating certain portions of the story.

The development of chemical principles is regarded in this book from the position of to-day. The book is not an attempt to move through the past without knowing whereto the course of the science is tending. I do not try to deal with the principles of chemistry in chronological order; I have arranged them in what seems to me the order of their interdependence, as that is judged from the "specular mount" whereon we now stand. I do not think it is possible to say of many chemical generalizations that they were appreciated and acted on from this or that year. There were times of advance and times of going back.

What classification of the principles of chemistry shall be adopted depends on what is now taken to be the purpose of the science. An examination of the progress of chemistry at different times, in the light of the knowledge we have to-day, seems to me to show that the main purpose of the science has always been the same. Chemistry has concerned itself in the past, as it concerns itself now, with the changes of material things; and, although the aspects of this study have been as varied as those of the transmutations of matter wherewith it deals, the essential object of the study, at all times, may be expressed in the language of to-day as being to describe, to set in due order, and to connect the changes of composition and the changes of properties which occur simultaneously in systems of homogeneous substances, and the conditions under which these changes proceed. The history of the advances which have been made towards attaining this object is the history of the principles of chemistry.

The actions of our surroundings on our senses are spoken of as the properties of substances. If all the properties, except, it may be, the masses of any portions of a substance obtained by sifting or sorting that substance are the same,

the substance is said to be homogeneous. From some homogeneous substances others have been produced which differ in properties from one another and from the original substance, and the sum of the masses whereof is equal to the mass of the original substance. Other homogeneous substances have been so changed that the mass of the product (or the mass of each product, if there is more than one) is greater than the mass of the original substance changed into that product. In other words; there are homogeneous substances which have been separated into unlike parts, and there are other homogeneous substances which have not been separated into unlike parts, but have been changed by combining them with substances different from themselves. These statements recognize different degrees of homogeneity.

What is meant in chemistry by the expression, " a homogeneous substance "? In other words, what is " a chemically distinct substance "? What happens when chemically distinct substances interact? These are the two main questions of chemistry; and these have always been the two main questions of chemistry, although the forms wherein these questions have been stated have differed much at different times.

To trace the forms which the two fundamental inquiries of chemistry have presented at different periods, to describe some of the methods which have been used to find answers to these inquiries, and to set forth the general results of the applications of these methods, is the object of this book.

Chemistry began to take shape as a definite branch of natural science in the seventies of the eighteenth century; my attempt to trace in detail the history of the principles of chemistry will begin with a consideration of the leading conceptions which guided chemical investigations about the year 1770; and, in order that the reader may grasp the position wherein the science was about that time, I will preface that fuller consideration by a short account of the progress of chemical conceptions from early times to the time of Lavoisier.

The subject proper of this book will be dealt with broadly as follows.

I. The history of the attempts to answer the question, What is a homogeneous substance?

> The recognition of homogeneous substances, and the description of chemical changes as the interactions of these substances;
>
> The marks of elements and of compounds;
>
> The laws of chemical combination, the atomic hypothesis, the molecular and atomic theory;
>
> The more searching examination of the compositions of homogeneous substances, allotropy;
>
> Elements which do not react;
>
> Chemical nomenclature and notation.

II. The history of the attempts to answer the question, What happens when homogeneous substances interact?

> The classification of homogeneous substances;
>
> Acids, bases, salts;
>
> Radicals, types, dualism, the unitary hypothesis;
>
> Chemical equivalency;
>
> Isomerism and constitutional formulæ;
>
> Application of the hypothesis of ionization to the classification of homogeneous substances;
>
> The periodic law;
>
> The conditions and general laws of chemical change;
>
> Chemical affinity;
>
> Chemical equilibrium;
>
> The elucidation of chemical reactions by measurements of physical properties.

TITLES OF JOURNALS REFERRED TO IN THIS BOOK.

ABBREVIATED TITLE.	FULL TITLE.
Abhand. der math.-phys. Classe der Königl. Säch. Gesell. Wiss.	Abhandlungen der mathematisch-physikalischen Classe der Königlich Sächsischen Gesellschaft der Wissenschaften. [1852 onwards].
Annal. Chem. Pharm.	Liebig's Annalen der Chemie und Pharmacie. [1840 onwards.]
Annal. Chim. Phys.	Annales de Chimie et de Physique. [Series 2 to 7, 1816 onwards.]
	Annales de Mines. [Series 4 to 9, 1842 onwards.]
	Annals of Philosophy. [1813–1821.]
Archiv. néerland.	Archives néerlandaises des Sciences exactes et naturelles. [1866–68; 1877–1881.]
Berichte.	Berichte der Deutschen Chemischen Gesellschaft. [1868 onwards.]
Brit. Ass. Reports.	Reports of the British Association for the Advancement of Science. [1831 onwards.]
Bull. de l'Acad. royale de Belgique.	Bulletin de l'Académie royale des Sciences, des Lettres, et des Beaux-Arts de Belgique. [1852 onwards.]
Bull. Soc. Chim.	Bulletin de la Société Chimique de Paris. [Series 1 to 3, 1863 onwards.]
Chem. News.	The Chemical News. [1860 onwards.]
C. S. Journal.	Journal of the Chemical Society. [1841 onwards.] See *Quart. Journ. C. S.*
Compt. rendus.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences. [1835 onwards.]
Gilbert's Annal.	Gilbert's Annalen der Physik und Chemie. [1799–1824.]
Jahresbericht.	Jahresberichte über die Fortschritte der Chemie, etc. [1857 onwards.]
Journal de physique.	Journal de Physique théorique et appliquée. [Series 1 to 4, 1872 onwards.]
J. phys. Chemistry.	Journal of Physical Chemistry. [1896 onwards.]

ABBREVIATED TITLE.	FULL TITLE.
J. prakt. Chem.	Journal für praktische Chemie. [Series 1 and 2, 1834 onwards.]
Kong. Sven. Vet.-Akad. Hand.	Kongliga Svenska Vetenkaps-Akademien Handligar. [1849 onwards.]
Mém. de l'Acad. des Sciences.	Mémoires de l'Académie Royale des Sciences de l'Institut de France. [1816 onwards.] Also: Les mémoires de mathematique et de physique. [1699–1790.]
Mém. de l'Acad. royale de Belgique.	Mémoires de l'Académie imperiale et royale des Sciences et Belles-Lettres de Bruxelles. [1784–1859.] After 1859 called Mémoires de l'Académie royale des Sciences, des Lettres, et des Beaux-Arts de Belgique.
Mém. de la Soc. d'Arcueil.	Mémoires de Physique et de la Chimie de la Société d'Arcueil. [1807 to 1817.]
	Nature. [1870 onwards.]
	Nicholson's Journal. [1801–1814.]
Phil. Mag.	Philosophical Magazine. [Series 1 to 6, 1814 onwards.]
Phil. Trans.	Philosophical Transactions of the Royal Society. [1744 onwards.]
Pogg. Annal.	Poggendorff's Annalen der Physik und Chemie. [1824–1876.]
Quart. Journ. C. S.	Quarterly Journal of the Chemical Society. (During the first eight years of the Chemical Society, its Journal was called *Memoirs and Proceedings;* for the next fourteen years it was called *Quarterly Journal;* after that it was named *Journal of the Chemical Society.*)
Quart. J. of Science.	Quarterly Journal of Science. [1864–1885.]
Rec. trav. chim. Pays-Bas.	Receuil des travaux chimiques des Pays-Bas et de la Belgique. [Series 1 to 2, 1882 onwards.]
Silliman's Amer. J.	American Journal of Science and Arts. (Called *American Journal of Science* since 1880.) [Series 1 to 4, 1843 onwards.]
Wied. Annal.	Wiedemann's Annalen der Physik und Chemie. [1877–1899.]
Zeitsch. für anorgan. Chemie.	Zeitschrift für anorganische Chemie. [1892 onwards.]
Zeitsch. für Chemie.	Zeitschrift für Chemie. [Series 1 and 2, 1858 to 1871.]
Zeitsch. für Krystallog.	Zeitschrift für Krystallographie und Mineralogie. [1877 onwards.]
Zeitsch. für physikal. Chemie.	Zeitschrift für physikalische Chemie. [1887 onwards.]

TABLE OF CONTENTS.

xiii

CHAPTER III.

The Marks of the Two Classes of Chemically Distinct Substances, Elements and Compounds. The Laws of Chemical Combination; and the Daltonian Atomic Theory.

CHAPTER IV.

The Differentiation of the Atom and the Molecule. The Determination of Atomic and Molecular Weights.

CHAPTER V.

The Determination of Molecular Weights Founded on the Measurements of Certain Physical Properties of Dilute Solutions, and the Extension of Avogadro's Law to these Solutions.

CHAPTER VI.

The More Searching Examination of the Composition of Homogeneous Substances. Allotropy.

CHAPTER VII.

Elements which do not React. Argon and its Companions.

APPENDIX.

PART II.

THE HISTORY OF THE ATTEMPTS TO ANSWER THE QUESTION, WHAT HAPPENS WHEN HOMOGENEOUS SUBSTANCES INTERACT?

SECTION I.

THE HISTORY OF THE CLASSIFICATION OF HOMOGENEOUS SUBSTANCES.

CHAPTER VIII.

Acids; Bases; Salts. Acid-forming and Base-forming Elements. Acidic and Basic Oxides.

CHAPTER IX.

Radicals. Types. Dualism and the Unitary Hypothesis.

CHAPTER X.

Chemical Equivalency.

CHAPTER XI.

Molecular Structure. Isomerism. Constitutional Formulæ.

CHAPTER XII.

Applications of the Hypothesis of Ionization to the Classification of Homogeneous Substances.

CHAPTER XIII.

The Periodic Law.

SECTION II.

THE HISTORY OF THE STUDY OF THE CONDITIONS AND GENERAL LAWS OF CHEMICAL CHANGE.

CHAPTER XIV

Chemical Affinity.

CHAPTER XV.

Chemical Equilibrium.

CHAPTER XVI.

The Elucidation of Chemical Reactions by Measurements of Physical Properties.

SECTION I.

RELATIONS BETWEEN CHANGES OF COMPOSITION AND CERTAIN OPTICAL PROPERTIES OF SUBSTANCES.

SECTION II.

RELATIONS BETWEEN CHANGES OF COMPOSITION AND THERMAL CHANGES.

A HISTORY OF

CHEMICAL THEORIES AND LAWS.

PART I.

THE HISTORY OF THE ATTEMPTS TO ANSWER THE QUESTION, WHAT IS A HOMOGENEOUS SUBSTANCE ?

CHAPTER I.

A SKETCH OF THE PROGRESS OF CHEMICAL CONCEPTIONS FROM EARLY TIMES TO THE DISCOVERY OF OXYGEN.

CHEMISTRY is a universal science; it was founded by many whose memories are forgotten. The foundations of chemistry are laid deep in the experiences, the hopes, the visions of mankind.

Certain ancient writers tell that such arts as dyeing, working in metals, making ornaments of precious stones, extracting essences and tinctures from plants, and the like, were taught to mankind by those "Sons of God [who] saw the daughters of men that they were fair, and took them wives of all which they chose." I suppose we should translate this myth into the language of to-day by saying that the use of chemical processes is to be traced to the primal necessities and instincts of human intelligence.

In his book, *Les Origines de l'Alchimie*,[1] Berthelot says:

"Chemistry is not a primitive science, like geometry or astronomy; it is constructed from the debris of a previous scientific formation; a formation half chimerical and half positive, itself founded on the treasure slowly amassed by the practical discoveries of metallurgy, medicine, industry, and domestic economy. It has to do with alchemy, which pretended to enrich its adepts by teaching them to manufacture gold and silver, to shield them from diseases by the preparation of the panacea, and finally to obtain for them perfect felicity by identifying them with the soul of the world and the universal spirit."

The practice, even in a crude way, of what are now called chemical industries must have accustomed the workers in these handicrafts to many striking transmutations, and suggested such questions as these: Do all things change? Are there limits to the changes we can effect? Can we, by seeking, discover the order and the method of these transformations?

The answers given by the Greek philosophers, about 500 B.C., to such inquiries were somewhat as follows. All things are formed of four elements; earth, air, fire, water. As experience shows that these elements are changeable, they must be formed of things less mutable than themselves. These less mutable things are indivisible, indestructible atoms. All material changes are changes in the combinations, separations, and positions of atoms. Atoms differ in size, weight, and shape. Round atoms, such as those of fire and those of the soul, move more freely than atoms of other shapes. The resistance which every atom offers to penetration by other atoms causes oscillatory movements which are communicated from atom to atom. The actual physical world is an assemblage of combinations of atoms; this assemblage is orderly, it is not many things ($\pi o \lambda \lambda \acute{\alpha}$), but a harmony ($\kappa \acute{o} \sigma \mu o s$). As atoms are indestructible, the total number of them is always the same; there is no destruction, as there is no creation of matter. Like atoms are drawn to like; for instance, some of the atoms which compose bread, water, and other kinds of food are identical with some of those whereof blood, muscles, and tissues are formed; hence our bodies are nourished by bread, water, and other foods.

---

[1] Paris, Georges Steinheil, 1885.

The answer given by the early Greek philosophers to the questions suggested by observation and experience of the changes of material things was a comprehensive theory of these changes. But, although comprehensive, the theory was not applicable directly and specifically to particular instances of transformations, so as to enable the likenesses between these to be measured, and the constant relations between them to be stated in quantitative expressions. Perhaps it would be more correct to say that the theory could not be applied to special cases of transformations until these had been examined quantitatively, and the relations between them expressed numerically. It is often asserted that the atomic theory of the Greek philosophers was purely speculative, that it rested on no foundation of observed or experimentally determined facts. Hoefer [1] has done well to remind us that there were in ancient Greece workshops of smiths, metallurgists, painters, and the like; and that some of the authors of the atomic theory were initiated into the *sacred art* of Egypt, which was nothing else than experimental chemistry, hidden from the vulgar under signs and symbols. We should remember also that only fragments of the writings of the founders of the atomic theory have come to us, embedded in less ancient books. It is at least possible that those who framed the Greek form of the atomic theory had a wider acquaintance with chemical facts than we are inclined, at first sight, to allow. What is left to us of Greek sculpture testifies that many Greeks were extraordinarily close observers of nature, and unsurpassable in their power of describing the facts which they observed. It is certainly true that when the Greek theory was revived, after more than two thousand years, and was made immediately applicable to facts established by quantitative experiments, that theory became the most fruitful conception which has yet been brought into chemistry.

"It is in the first centuries of the Christian era that we find the traces of a science that appears to be new, although it is really very old. In the Greek manuscripts which we shall consider it is called *the sacred science* . . . or *the divine and sacred art*. That sacred science or divine art, which had no particular name throughout antiquity, was chemistry." [2]

[1] *Histoire de la Chimie* (vol. i, p. 103), par Ferdinand Hoefer. [2d ed., Paris, 1866; Firmin Didot Frères, Fils et Cie.]
[2] Hoefer, vol. 1, p. 225.

In the early centuries of the Christian era life was more sombre and less harmonious than in the days of the Greeks. Fearless delight in living was being exchanged for a brooding sense of mystery; miracle and magic were taking the place of intellectual speculation.

Working in metals and other processes, wherein specific substances seemed to go out of existence and others to be created in their places, began to be looked on as encroachments on the powers of the Creator, as dangerous wanderings from the ordered paths whereby alone legitimate knowledge could be gained. But such processes were fascinating; they were fascinating to the speculative intellect, and attractive to the practical instincts of men, because they might lead to methods for changing the inferior metals into gold, that is to say, to methods for gaining power and pleasure. In these centuries there was a considerable amount of knowledge of chemical manufactures; but the receipts for conducting these manufactures which have come to us are constantly mixed with directions for performing magical processes. Expiring paganism collected weapons from all armouries; to those which it drew from the mystical doctrines of Egypt, where *the sacred art* had long been practised, the Christian apologists opposed the weapon of their own mysticism. Hence sprung a strange and hybrid crop of doctrines. Berthelot (*l. c.*, p. 2) says that alchemy rested partly on the industrial processes of the ancient Egyptians, partly on the speculative theories of the Greek philosophers, and partly on the mystical reveries of the Gnostics and the Alexandrians.

A theory of the world was gradually developed on the fundamental conception of the unity of all things. Beneath the changes which seem to occur everywhere and in everything, there must be, it was said, some unchanging and unchangeable essence. A hidden thread of unity must run through all phenomena. To find that unchangeable essence, to discover that secret binding unity, became the quest of alchemy,[1] the art which rested on the conception of *the one and the all*. If *the one*

---

[1] I do not propose to discuss the origin of the names *chemistry* and *alchemy*.

thing was found, the method of its discovery was to be kept hidden; partly because of the punishment which is always inflicted by men on those who eat of the fruit of the tree of knowledge, partly because of the dread of the divine anger. "What men write," says an ancient MS., "of that are the divinities jealous." (Quoted by Berthelot, *l. c.*, p. 25.)

Most of the changes we notice, or are able to produce, were regarded by the alchemists as superficial, as changes in the outer coverings of an all-pervading reality: beneath the wrappings which are put off and on, there exists, they said, an essence which abides and is unchangeable. Water, air, earth, and fire were regarded by many alchemists as the most firmly clinging vestments of this unchangeable essence; cold, heat, moistness, dryness, and the like, were classed among the more easily removed coverings of the essence. Stephanus of Alexandria (about 620 A.D.) said: [1]

"It is necessary to deprive matter of its qualities in order to draw out its soul. . . . Copper is like a man; it has a soul and a body; . . the soul is the most subtile part, . . . that is to say, the tinctorial spirit. The body is the ponderable, material, terrestrial thing, endowed with a shadow. . . . After a series of suitable treatments copper becomes without shadow and better than gold."

Stephanus says, that to drive away the shadow from matter, substances must be destroyed, put to death, and then raised in their proper, pure, and immaculate nature. "The elements," he tells us, "grow and are transmuted, because it is their qualities, not their substances, which are contrary." The same Neo-Platonist says that if copper is to receive the power of colouring other substances, such as glass and enamels, it must first be itself destroyed by dissolution. We have here an example of the connexion between the industrial processes used by the alchemists and their general theory of the changes of matter; the theory gave a ground for the industry, and the industry confirmed the theory.

The sentence quoted,

"It is necessary to deprive matter of its qualities in order to draw out its soul,"

---

[1] Quoted by Berthelot (*l. c.*, pp. 276, 277), from a MS. in Greek, in the *Bibliothèque Nationale* at Paris.

contains the whole theory of alchemy. Substances were thought of as things distinct from their qualities; as things whose real nature was concealed by their envelopes and did not become apparent until these envelopes, which were the qualities of the substances, had been destroyed. The alchemists taught— it would probably be more correct to say, were inclined to teach—that all substances are formed of the same fundamental entity, but it is easier to remove the particular qualities of some substances than those of others.

"There abides in nature a certain form of matter which, being discovered and brought by art to perfection, converts to itself, proportionally, all imperfect bodies that it touches."

What Berthelot says of this doctrine is true:

"It rested on the indisputable appearance of an indefinite cycle of transformations, reproducing themselves in chemical operations, without either beginning or end." (*L. c.*, p. 283.)

The alchemical conception of different substances as forms of *the one thing*, that is, portions of the same entity concealed in different wrappings, prevailed throughout the Middle Ages, and did not wholly disappear until towards the end of the eighteenth century. That the language which grew out of alchemical ways of thinking has not yet been altogether abandoned, is shown by phrases which sometimes occur in the text-books and examination-papers of to-day; such phrases, for instance, as these: *iron exists in nature in the form of hæmatite; explain the tendency of nitrogen to pass into the form of nitrates; water and hydrogen peroxide both contain the elements hydrogen and oxygen.* Such names as *aqua fortis, aqua regia,* and *strong waters* (used in the British Customs Tariff), are remnants of the time when the properties of a substance were thought of as clothes which could be put off and on, or exchanged for others, without destroying the essential nature of the substance.

There are expressions now in common use which must be survivals, I suppose, of the alchemical way of assigning moral virtues and vices to material things. We speak alchemically, not scientifically, when we say: *copper is a good conductor of electricity, sulphur conducts heat badly, gases obey the gaseous*

laws, these events are governed by such or such a ˙aw, or hydro-gen is a nearly perfect gas. About two hundred and fifty years ago Boyle said (in his *Reflections upon the Hypothesis of Alcali and Acidum*):

"Those hypotheses do not a little hinder the progress of humane knowl-edge, that introduce morals and politicks into the explications of corporeal nature, where all things are indeed transacted according to laws mechanical."

The conception of the unity of material things has never dis-appeared from chemical science; it has been revived in our own times, and the experimental basis of it has been strengthened.

As knowledge of chemical processes advanced, and especially as chemical industries increased, it became necessary to classify the many and diverse substances that were discovered. The general theory that all substances were forms of *the one thing* which was more completely hidden by the qualities of some sub-stances than by those of others, was made directly applicable to specific cases by supposing that like substances contained certain common principles. The properties peculiar to specified substances were regarded as crusts which could be removed without much difficulty; as houses which must be destroyed if the vivifying spirit that dwelt therein were to go free. To remove these incrustations, which were thought of as accidental and belonging only to individuals, was to take the first step towards the attainment of the underlying unity. When sub-stances had been stripped of their peculiar properties there were still differences between them; but it was possible to sort them into classes, putting together those which were broadly alike, and separating those which were distinctly unlike. Like sub-stances were supposed by the alchemical theory to resemble one another because they contained one, or more than one common principle. The goal was attained when the principles common to many substances had been removed; then at last appeared *the one thing* which contained in itself, and itself was, the essential principle of all imperfect things, the *heavenly rain*, the *water of paradise*, the *virgin and blessed water*, the *old dragon*, the *carbuncle of the sun*. By obtaining a mastery over the principles of things a man was able to accomplish many minor transformations; but to be master of the *Stone of Wisdom*—

which was "youthful and ancient, weak and strong, life and death, visible and invisible, hard and soft, most high and most low, light and heavy"—was to have the power of performing all transmutations. The alchemical theory thought of a substance as having a threefold nature; some portion of the universal essence, this essential thing with a covering of principles, and these with an outer wrapping of specific properties. A substance was pictured to himself by the alchemist as formed mediately from the universal essence, and immediately from principles, which were sometimes called elements. Certain alchemists seem to have regarded these principles, or elements, as themselves derived from more pure, less compounded, elements. This conception of the threefold nature of substances is found running through many alchemical writings. The English adept, Thomas Vaughan (who wrote in the middle of the seventeenth century under the name Eugenius Philalethes), translating from "the oracle of magick, the great and solemn Agrippa," says:

"There are then four Elements, without the perfect knowledge of which we can effect nothing in Magick. Now each of them is threefold—of the first order are the pure Elements, which are neither compounded, nor changed, nor admit of mixtion, but are incorruptible, and not of which but through which the vertues of all naturall things are brought forth into act. No man is able to declare all their vertue because they can do all things upon all things. . . . Of the second order are elements that are compounded, changeable, and impure, yet such as may by art be reduced to their pure simplicity, whose vertue, when they are thus reduced to their pure simplicity, doth above all things perfect all occult and common operations of Nature, and these are the foundations of the whole naturall Magick. Of the third order are those elements which originally, and of themselves are not elements, but are twice compounded, various, and changeable one into the other. They are the infallible medium, and therefore are called the middle nature, or Soul of the middle nature. . . . In them is . . . the perfection of every effect in what thing soever, whether naturall, cœlestiall, or supercœlestial; . . . . for from these, through them, proceed the bindings, loosings, and transmutations of all things. . . . Whosoever shall know how to reduce those of one order into those of another, impure into pure, compounded into simple, and shall know how to understand distinctly the nature, vertue, and power of them in number, degrees, and order, without dividing the substance, he shall easily attain to the knowledge and perfect operation of all naturall things, and cœlestiall secrets."

The alchemical principles, or elements, "of a middle nature,"

sometimes named salt, sulphur, and mercury, sometimes arsenic, sulphur, and mercury, were not thought of as substances, in the modern connotation of that word; at any rate, they were not so thought of in the earlier periods of alchemy. They were qualities, not qualities of individual substances, but of classes of substances, and they could be detached from the substances which were the vehicles of their exhibition. I think we may perhaps best translate the alchemical expressions *principles of a middle nature*, and *elements of a middle nature*, by the term *class-marks*.

"The life of metals," said Paracelsus, "is a secret fatness; of salts, the spirit of *aqua fortis;* of pearls, their splendour; of marcasites and antimony, a tingeing metalline spirit; of arsenics, a mineral and coagulated poison."

The alchemists taught that what nature did slowly in her own way men might do more quickly in their workshops. Gradually and without haste, nature removed the particular qualities of some substances; the products of these natural changes were sometimes identical, although the substances wherewith the processes began had been very different. In Ben Jonson's *Alchemist*, when Surly, who is not to be cozened into accepting Subtle's tricks as genuine, is arguing with Subtle about the transmutation of metals, we read:

Subtle. No egg but differs from a chicken more
       Than metals in themselves.
Surly. That cannot be.
       The egg's ordained by nature to that end
       And is a chicken *in potentia*.
Subtle. The same we say of lead and other metals,
       Which would be gold if they had time.

       .   .   .   .   .   .
       . . . for 'twere absurd
       To think that nature in the earth bred gold
       Perfect in the instant; something went before.
       There must be remote matter.

The final step to perfection, the tearing away the principles, or elements (the general qualities), of similar or even apparently identical substances, was to be accomplished by the art of man. As the particular qualities of some substances could be removed more easily than those of others, and as the principles, or elements, of some classes of substances could be taken away

more readily than the principles of other substances, the first
aim of the alchemist in seeking to gain the *essence* was to find
the most suitable substance wherewith to begin the series of
operations which might culminate in the great transmutation.
Hence the strange ingredients that were thrown into the fur-
nace, for the perfecting of *the Stone*. In *The Alchemist* Surly
flouts Subtle, and scornfully flings in his face

> Your stone, your medicine, and your chrysosperme,
> Your sal, your sulphur, and your mercury,
> Your oil of height, your tree of life, your blood,
> Your marchesite, your tutie, your magnesia,
>
> .   .   .   .
>
> And then your red man and your white woman,
>
> .   .   .   .
>
> Hair o' the head, burnt clouts, chalk, merds, and clay,
> Powder of bones, scaldings of iron, glass,
> And worlds of other strange ingredients
> Would burst a man to name.

The things that are formed by the action of fire on many ordinary
substances seem to be simpler than the original substances;
hence the constant use of the furnace and the alembic by the
alchemists for driving out both the particular and the general
properties of substances, and thereby, as they thought, reducing
substances to their primal, simple essence.

At a later time, a principle, or an element, was regarded,
sometimes as a general quality of a class of substances, some-
times as a condition or state of many substances, sometimes as
the process of passing into a certain state or condition, and
sometimes as a particular substance. Take the word *water*, for
instance. Berthelot (*l. c.*, p. 268) points out that in alchemical
writings this word meant: (I) the hypothetical element whose
union with bodies caused them to become liquid, or (II) a par-
ticular liquid or liquefiable substance such as water or a fusible
metal, or (III) the state or condition of liquefied substances, or
(IV) the act of liquefaction in general.[1]   These modifications of
the conception of principle, or element, brought new difficulties.

---

[1] Berthelot (*l. c.*, p. 267) says, truly, that even in the nineteenth century the word
fire has been employed to mean the supposed imponderable element of fire (caloric),
or the matter of a burning body (" do not touch the fire "), or the actual state
of a body undergoing combustion (" the house seemed to be on fire "), or the
act of combustion (" setting on fire," " to put out the fire ").

In the seventeenth century we find many students of natural changes protesting against the vague, varying, and elusive meanings of such expressions as *the mercurial principle*, the *principle of fixed sulphur*, and the like. Kunckel (1630–1702) cries out in despair:

"I, old man that I am, occupied with chemistry for sixty years, have not yet been able to discover what is their *Sulfur fixum*, and how it forms a definite part of metals." [1]

Kunckel complained bitterly of the alchemists' habit of giving different names and different properties to the same substance.

"The ancients," he says, "were not agreed about the kinds of sulphur. The sulphur of one is not the sulphur of another, to the great injury of science. To that one replies that every one is perfectly free to baptize his infant as he pleases. Granted. You may, if you like, call an ass an ox, but you will never make any one believe that your ox is an ass." [2]

Boyle, referring to the vague, loose, cumbrous writers on chemistry of his time, exclaims in *The Sceptical Chymist* (published 1678–9):

"If judicious men, skilled in chymical affairs, shall once agree to write clearly and plainly of them, and thereby keep men from being stunned, as it were, or imposed upon by dark and empty words; it is to be hoped, that these [other] men finding, that they can no longer write impertinently and absurdly, without being laughed at for doing so, will be reduced either to write nothing, or books, that may teach us something, and not rob men, as formerly, of invaluable time; and so ceasing to trouble the world with riddles or impertinencies, we shall either by their books receive an advantage, or by their silence escape an inconvenience." [3]

A great reduction in the number of principles was effected in the first quarter of the eighteenth century by the invention of the one, comprehensive *principle of phlogiston*. Before giving a sketch of the phlogistic theory, and mentioning some of the effects thereof on the progress of chemistry, I wish to ask the reader's attention to the views on the principles, or elements, of the alchemists, enunciated by Boyle, a man of singularly clear and penetrative intellect. The Honourable Robert Boyle, son of the Earl of Cork, was born in 1626 (the year in which Bacon

---

[1] Quoted by Hoefer, *l. c.*, vol. ii. p. 198.

[2] *Ibid.*

[3] The orthodox view in Boyle's time was that all substances are made of a sulphurous, a saline, and a mercurial part—these being the three active principles—with more or less of some, or all, of the five things (sometimes called principles), salt, spirit, oil, phlegm (which included water), and earth.

died), and died in 1691.   (The treatise by Stahl, which developed
the theory of phlogiston, was not published until 1717.)   The
alchemists (or, as Boyle called them, the *vulgar Peripateticks*,
and *vulgar Spagyrists*) regarded fire as the great simplifying
agent; by repeated heatings, sublimations, cohobations, and
calcinations, the true, inner kernel, they said, would at last be
revealed.   Boyle combatted this opinion.   He showed that the
effects of fire on the same substance differ according to the con-
ditions.   In *The Sceptical Chymist* [1] he says that when guiacum
is heated in an open fire it yields ashes and soot, but when heated
in a retort it gives oil, spirit, vinegar, water, and charcoal.   Of
the effects of heating common brimstone, he says:

"Exposed to a moderate fire in subliming pots, it rises all into dry, and
almost tasteless, flowers; whereas being exposed to a naked fire, it affords
store of a saline and fretting liquor."   The general effect of fire was described
by Boyle (*l. c.*) in these words : "The fire, even when it divides a body
into substances of divers consistencies, does not most commonly analyze
it into hypostatical principles, but only disposes its parts into new textures,
and thereby produces concretes of a new indeed, but yet of a compound
nature."

He noticed that the effect of strongly heating some substances
was to produce others which weighed more than the original
substances; and he supposed that this was due to the com-
bination of the matter of fire with the substances which were
calcined.   In *New Experiments to make Fire and Flame stable
and ponderable,* Boyle commends to the study of philosophers
this "subtil fluid," which is "able to pierce into the compact
and solid bodies of metals" (he had heated weighed quantities
of tin, lead, and other metals), and "can add something to
them that has no despicable weight upon the balance, and is
able for a considerable time, to continue fixed in the fire."
The *vulgar Spagyrists* often mixed the substances, which were
to be broken up by heating, with other things, before subjecting
them to the action of fire; on this Boyle makes the pregnant
remark:

"Whenever any menstruum or other additament is employed, together
with the fire, to obtain a sulphur or a salt from a body, we may well take

---

[1] Published 1678–9; with the sub-title, "*Chymico-physical Doubts and Para-
doxes touching the experiments whereby vulgar Spagyrists are wont to endeavour to
evince their Salt, Sulphur, and Mercury, to be the true principles of things.*"

the freedom to examine, whether or no the menstruum do barely help to separate the principle obtained by it, or whether there intervene not a coalition of the parts of the body wrought upon with those of the menstruum, whereby the produced concrete may be judged to result from the union of both." Hence, he says, "It is not so sure that every seemingly similar or distinct substance that is separated from a body by the help of the fire, was pre-existent in it, as a principle or element of it." [1]

Boyle thought that there may be very good "openers of compound bodies" besides fire; he says he has seen experiments which argue strongly that there may be ways of dealing with compound bodies which "leave them more unlocked than a wary naturalist would easily believe."

Many of Boyle's remarks on experiments, explanation of natural occurences, and theories, are very admirable. How good it would be, if *wary naturalists* always acted in the spirit of what Boyle says in *Some considerations touching experimental essays in general*:

"That then, that I wish for, as to systems, is this, that men in the first place, would forbear to establish any theory, till they have consulted with . . . a considerable number of experiments, in proportion to the comprehensiveness of the theory to be erected on them. And, in the next place, I would have such kind of superstructures looked upon only as temporary ones; which though they may be preferred before many others, as being the least imperfect, or, if you please, the best in their kind that we yet have, yet are they not entirely to be acquiesced in, as absolutely perfect, or uncapable of improving alterations."

Boyle had no great opinion of the methods of the chemists of his time.

"Methinks the Chymists, in their searches after truth, are not unlike the navigators of *Solomon's Tarshish* fleet, who brought home from their long and tedious voyages, not only gold, and silver, and ivory, but apes and peacocks too: for so the writings of several (for I say not, all) of your hermetick philosophers present us, together with divers substantial and noble experiments, theories, which either like peacocks feathers make a great show, but are neither solid nor useful; or else like apes, if they have some appearance of being rational, are blemished with some absurdity or other, that, when they are attentively considered, make them appear ridiculous." [2]

What could be more just than the following remarks (in *Considerations touching experimental essays in general*):

"I consider then, that generally speaking, to render a reason of an effect or phenomenon, is to deduce it from something else in nature more known than itself; and that consequently there may be divers kinds of degrees

---

[1] *Sceptical Chymist.*   [2] *Ibid.*

of explication of the same thing." He praises "those heroick wits that do so much as plausibly perform something," in trying to deduce "the chiefest modes or qualities of matter, from the more primitive and catholick affections of matter, namely, bulk, shape, and motion." "But," he adds, "I think too, we are not to despise all those accounts of particular effects, which are . . . deduced . . . from the familiar, though not so universal, qualities of things, as cold, heat, weight, hardness, and the like." "It ought to be esteemed much less disgraceful," he says, "to quit an error for a truth than to be guilty of the vanity and perverseness of believing a thing still, because we once believed it. And certainly, till a man is sure he is infallible, it is not fit for him to be unalterable."

I suppose there was no opinion regarding external nature thought by Boyle's contemporaries to be more just and well-grounded than that which assigned to each substance a condition, or mode of existence, *natural* to that substance, and regarded any departure from that condition as caused by some violent, or non-natural means. It would not, I think, be too much to say that large theories of morality, and many rules of conduct, have been founded, and are still founded on this supposition. By going strongly against this view, and showing the crudity of it, both by experiments and reasoning, Boyle proved himself far in advance of the naturalists of his time.

In *A Paradox of the natural and preternatural state of Bodies, especially of the Air*, Boyle says:

"I know, that not only in living, but even in inanimate bodies, of which alone I here discourse, men have universally admitted the famous distinction between the natural and preternatural, or violent state of bodies, and do daily, without the least scruple, found upon it hypotheses and ratiocinations, as if it were most certain, that what they call nature, had purposely framed bodies in such a determinate state, and were always watchful, that they should not by any external violence be put out of it. But notwithstanding so general a consent of men in this point, I confess, I cannot yet be satisfied about it in the sense wherein it is wont to be taken. It is not, that I believe, that there is no sense, in which, or in the account upon which, a body may be said to be in its natural state; but that I think the common distinction of a natural and violent state of bodies has not been clearly explained, and considerately settled, and both is not well grounded, and is oftentimes ill applied. For, when I consider, that whatever state a body be put into, or kept in, it obtains or retains that state, assenting to the catholick laws of nature, I cannot think it fit to deny, that in this sense the body proposed is in a natural state; but then, upon the same ground it will be hard to deny, but that those bodies, which are said to be in a violent state, may also be in a natural one, since the violence they are presumed to suffer from outward agents, is likewise exercised no otherwise than according to the established laws of universal nature."

The views held by Boyle regarding elements, principles, and qualities may be gathered from the following quotations from *The Sceptical Chymist* and *Essays concerning the unsuccessfulness of Experiments*. He analyses carefully the methods for distinguishing a definite substance, such as water, from admixtures of it with other bodies; he shows that the tests of insipidity, want of odour, and fluidity are not delicate enough to distinguish, always, one kind of water from another. Even if one had "portions of matter," such that they could not be changed by fire, "nor the usual agents employed by chymists," "it would not necessarily follow that such permanent bodies were elementary." He notices the changes that lead undergoes by the action of fire and other agents (it may be opaque, transparent, malleable, brittle, etc.); and he remarks that to distinguish what substances are really elementary "is not so easy as chymists and others have hitherto imagined." Boyle was careful to point out that the same name was often given to many things which are really different; very different substances, for instance, were sold under the name *antimony*. He noticed the existence of silver in some lead ores, but not in others; and he said that different specimens of what was called *lead* might behave very differently in experiments.

"Some mineral bodies, which pass without dispute for minerals of such and such a precise nature, may have lurking in them minerals of quite other nature, which may manifest themselves in some particular experiments (wherein they meet with proportionate agents or patients) though not in others."

He remarks that people are ready to assign small differences between things which are alike "to any other cause rather than the unsuspected difference of the materials employed about them." In making the same preparation, sufficient care was not always taken, Boyle said, to have the conditions identical; the "menstruum" used might not be so "highly rectified, or otherwise as exquisitely depurated" in one case as in another.

"I . . . must not look upon any body as a true principle or element, but as yet compounded, which is not perfectly homogeneous, but is further resoluble into any number of distinct substances, how small soever." "I . . . mean by elements, as those chymists that speak plainest do by their principles, certain primitive and simple, or perfectly unmingled bodies;

which not being made of any other bodies, or of one another, are the ingredients of which all those called perfectly mixt bodies are immediately compounded, and into which they are ultimately resolved: now whether there be any one such body to be constantly met with in all, and each, of those that are said to be elemented bodies, is the thing I now question."

Concerning the usefulness of elements or principles, and the ways wherein they should be used, Boyle makes the following most admirable remarks:

"The main thing that has recommended the chymical principles to more discerning men, seems to be, that by the help of a few simple ingredients, . . . associated in differing proportions, all mixt bodies may be compounded; and so men may acquaint themselves with the natures of a multitude of bodies, by first knowing the natures but of a few." "It is now time, to consider not of how many Elements it is possible that nature may compound mixt bodies, but (at least, as far as the ordinary Experiments of Chymists will inform us) of how many she doth make them up."

With regard to *qualities*, the following quotation from *Suspicions about some hidden qualities in the Air* is clear and suggestive:

" And as by air I understand not (as the Peripateticks are wont to do) a mere elmentary body; so when I speak of the qualities of the air, I would not be thought to mean such naked and abstract beings (as the schools often tell us of), but such as they call qualities *in concrete*, namely, corpuscles endued with qualities, or capable of producing them in the subjects they invade and abound in."

Boyle was most plainly endeavouring to distinguish the qualities from the compositions of substances; he was feeling his way towards a more satisfactory and simpler method of stating what he meant by qualities and composition than was given either by the four elements of the *vulgar Peripateticks* or the three principles of the *vulgar Spagyrists*. How far he saw into the real relations of natural phenomena is evident from many of his writings, notably from the following (in *The Sceptical Chymist*):

"I am apt to think, that men will never be able to explain the phenomena of nature, while they endeavour to deduce them only from the presence and proportions of such or such material ingredients, and consider such ingredients or elements as bodies in a state of rest; whereas indeed the greatest part of the affections of matter seems to depend upon the motion and the contrivance of the small parts of bodies. For it is by motion, that one part of matter acts upon another; and it is for the most part, the texture of the body,

upon which the moving parts strike, that modifies the notion or impression, and concurs with it to the production of those effects which make up the chief part of the naturalist's theme."

In the three or five elements of the *vulgar Spagyrists* of his time, Boyle found the same faults as those which Lavoisier, about a hundred years later, found in the principle of phlogiston: they were always changing; there was no getting a firm hold of them; the differences which they indicated between substances were based on the most trivial properties; and they were neither helps towards comprehending facts nor guides in the discovery of facts.   Boyle did not deny the usefulness of principles as helps towards bringing into one point of view material changes which are really similar; but, before using these aids, he insisted on analyzing, experimentally and rationally, the actual processes of change.   One of his main objects was to state observed facts without using the distorting language of the alchemical principles, essences, and elements.   He knew that a vague and grandiose language acts like a magic mirror wherein one sees what one has been persuaded ought to be seen.   In his *Essays concerning the unsuccessfulness of Experiments* he says:

"I remember Mr. R. the justly famous maker of dioptical glasses, for merriment telling one that came to look upon a great tube of his of thiry foot long, that he saw through it in a mill six miles off a great spider in the midst of her web; the credulous man, though at first he said he discerned no such thing, at length confessed he saw it very plainly, and wondered he had discovered her no sooner."

Boyle insisted on accuracy and on quantitative experiments in chemistry; he showed the complexity of chemical occurences; he exposed not only the inaccurate experiments, but also the loose reasoning that were the vogue in chemistry in his day; he made constant use of common sense, but common sense made accurate and imaginative; he exercised a cautious scepticism; he refused to trust the results of single experiments; while he recognized the many sources of error in questioning nature, he had a well-grounded faith in the experimental method of inquiry; when he obtained different results under what seemed the same conditions, he attributed these differences to small variations in the conditions which he had overlooked, and he set himself to discover these variations and to remove them;

his was a large view of nature, and he recognized the interdependence of events which to a superficial observer seemed unconnected; and he took for granted the great importance to mankind of correct experiments and accurate reasoning on natural events. Of the great names that are written in the illustrious roll of English men of science, there are few greater than Robert Boyle.

The orthodox alchemist of the seventeenth century used the words *element* and *principle* in a loose and elusive manner, sometimes as exchangeable terms, sometimes with different, but undefined, meanings; and he asserted that there exists one fundamental principle (or element) which can be separated from "imperfect bodies," in all of which it is hidden, and can "by art be brought to perfection." Boyle, on the other hand, used the two words *elements* and *principles* as synonymous; as meaning definite substances, each having properties that distinguish it from all others, which being themselves "perfectly unmingled," that is, not made of any other bodies, can "be brought to afford" (to use his own cautious phrase) substances different from themselves, by being "immediately compounded" with other elements, and into which all "mixt bodies are ultimately resolved." As regards the existence of one "pure" element in all less pure substances, Boyle remarked, "whether there be any one such body" (that is, any one element, as defined by him), "to be constantly met with in all, and each, of those, that are said to be elemented bodies, is the thing I now question."

About forty years after the appearance of *The Sceptical Chymist*, Stahl published his work,[1] wherein was elaborated the theory of phlogiston, a theory which reduced the number of the alchemical principles, and for a time helped to simplify both the ideas and the language of chemistry. The *principle of phlogiston* was, however, an alchemical invention: looking back, we now see that compared with the lucid and clarifying conceptions of Boyle regarding elements, it was confused, confusing, and re-

---

[1] *Zufällige Gedanken und nützliche Bedenken über den Streit von den sogenannten Sulphure, und zwar sowohl dem gemeinen verbrennlichen oder flüchtigen, als unverbrennlichen oder fixen.* Halle, 1717.

tarding.   But the theory was in keeping with the spirit of the time; while maintaining the ideas that had prevailed for many centuries, it simplified these ideas and made them directly applicable to a class of changes that had always been peculiarly fascinating to chemists, the changes which occur when substances are heated.   As inquiry advanced, and new facts were discovered, for about sixty years the theory of phlogiston proved itself sufficiently elastic to cover most of the new facts, and with a little stretching, to give an explanation of them which did not demand the use of terms and ideas that were unfamiliar and, therefore, unwelcome.

More than one observer in the fourteenth and fifteenth centuries said that the calcination of metals was accompanied by the union of an aeriform substance with the metals; one at least, Paul de Canotanto, said that calcination was the destruction of the igneous principle.[1]   Stahl (1660–1734) adopted the second opinion, and on that basis developed a theory of combustion, which became at a later time a theory of chemical reactions.   In his *Chymia rationalis et experimentalis* (Leipzig, 1729), Stahl says:

"Die Chimie . . . ist eine Kunst, die gemischten, oder zusammengesetzten, oder zusammengehaüfften (*aggregata*) Cörper, in ihre *principia* zu zerlegen, oder aus solchen *principiis* zu dergleichen Cörper wieder zusammen zu fügen."

These words seem very like the statements in many textbooks of to-day concerning the purpose of chemistry.   But everything depends on what Stahl meant by resolving mixed or compounded bodies into their *principles;* a consideration of his principle of combustibility will show, I think, that he used the term *principles* after the loose, changeable, alchemical manner.

Stahl,[2] to some extent following Becher, whose disciple he professed to be, said that fire exists both in the state of com-

---

[1] Hoefer (*Histoire*, vol. i. p. 468) quotes from a MS. written by this alchemist, who probably lived in the fifteenth century.   Of calcination he said: *Calcinatio est metallorum incineratio, sive destructio igneitatis.*

[2] In the account I give of Stahl's phlogistic theory, I have followed Hoefer (*Histoire*, vol. ii. pp. 397–401), and Kopp (*Geschichte der Chemie*, vol. i. pp. 148–193).   Stahl's *Zufällige Gedanken* is very rare; most of his works are written in a strange jumble of Latin and German.

bination and in the free state.[1] All combustible bodies are combustible because they hold in themselves the principle of combustibility; when a body is burnt the principle of combustibility escapes; in its uncombined condition this principle is apparent to our senses, and we call it fire, or flame; combustion is the passage of combined fire into the condition of uncombined fire. Stahl (or some of his followers, according to Hoefer) gave the name *phlogiston* to the principle of combustibility, or combined fire ($\phi\lambda o\gamma\iota\sigma\tau o\varsigma$ = burnt, or set on fire). The component parts of a substance were finally reduced to two, by the theory of phlogiston; an inflammable principle (*phlogiston*), and another principle (or element) which varied according to the class to which the substance belonged.[2] The more easily burnt a substance is, the richer it is in phlogiston, according to this theory; as charcoal, phosphorus, sulphur, oils, and fats are very rich in this principle, they are most suitable for communicating phlogiston to other substances which are deficient therein. The upholders of the theory said that metals were composed of phlogiston, and an earthy matter which varied somewhat in different individual metals: the removal of phlogiston from a metal caused the earthy matter to become apparent; the addition of phlogiston to a calx, that is, the product of burning a metal, was the revivification of the metal. The theory of phlogiston regarded calcination as an analytical process, and reduction as a synthetical reaction. To the argument that, because the product of calcining a metal weighs more than the uncalcined metal, therefore the metal cannot have lost something in the process, the thoroughgoing upholder of the theory had two replies: sometimes he said "of course the calx weighs more than the metal, because phlogiston tends to lighten or buoy up a body which contains it, and

---

[1] This alchemical mode of expressing certain facts still prevails, to the detriment of accurate thinking.

[2] Stahl recognized three substances in the imperfect metals:

"*Sonsten ist aus den angeführten* alterationibus metallorum *zu notiren dass in den* metallis imperfectis *dreyerley* substantia *vorhanden sey:* (1) *eine* quasi superficialis cohesionis quæ et ea propter omnium prima abit, scilicet substantia inflammabilis seu $\phi\lambda o\gamma\iota\sigma\tau o\nu$; (2) substantia colorans, quæ apparet in coloratis horum metallorum vitris, *und endlich;* (3) substantia crudior, *und diese sonderlich* in den crassioribus metallis, *Eisen und Kupfer zu finden.*" (Quoted by Hoefer, *l. c.,* vol. ii., p. 396, note.)

therefore the body weighs more after it has lost its phlogiston"; sometimes his answer was, "loss or gain of weight is an accident, the essential thing is change of qualities."

The theory of phlogiston, in its earlier development at any rate, was very simple; by the help of a single assumption, it emphasized the fundamental similarity between all processes of combustion. As Hoefer remarks (*l. c.*, vol. ii. p. 399): "S'il est vrai que la simplicité est le caractère distinctif de la verité, jamais théorie n'aura été aussi vrai que celle de Stahl." Lavoisier, in *Réflexions sur le Phlogistique* (collected edition of his works, Paris, 1862, vol. ii. pp. 624–5), says that Stahl made two important discoveries: (1) that the calcination of metals is a true combustion, (2) that the property of being inflammable can be transmitted from one body to another.

By asserting, and to some extent experimentally proving the existence of one principle in a vast number of different substances, that is to say, one property common to all these substances, the phlogistic theory acted as a very useful means for collecting, and placing in a favourable position for closer inspection, many substances which would probably have remained scattered and detached from one another had this ingathering instrument not been constructed. On the other hand, the readiness wherewith the phlogistic machinery was set in motion, and its flexibility, encouraged loose observations, and tended to the neglect of quantitative experiments and searching analyses of chemical changes. As the conception of definite kinds of substances, and of chemical changes as actions and reactions between definite substances, gained clearness and strength, the upholders of the phlogistic theory were forced to invent many subsidiary hypotheses. Each addition made the machinery more complicated, until at last it refused to work. This process of complication and disintegration occupied about sixty years. For at least a couple of generations every chemical fact was presented in the language of the phlogistic theory.[1]

---

[1] Hoefer (*Histoire*, vol. i. p. 145), mentions that a French translator of Pliny, in the eighteenth century, rendered the words (referring to the marked inflammability of sulphur), " *Quo apparet ignium vim magnam etiam ei inesse,*" by the phrase, " *Ce qui fait voir que le soufre contient beaucoup de phlogistique.*"

And, so long as the qualities of substances were the important objects of study, the language was so simple, natural, and easily learnt that no more subtle mode of expression was required. Moreover, the expression of some quantitatively established facts in terms of this theory was found to be possible. Cavendish, who was a scrupulously accurate experimenter, and the very impersonation of the unimpassioned, critical intellect, lived and died a phlogistean; and several other great chemists, including Scheele, were strong upholders of the theory. A man of pre-eminent genius was needed to break the domination of phlogiston; Lavoisier was the man who led chemistry into a freer atmosphere.

To give some account of the work of Priestley on matters connected with combustion will be, perhaps, the best way both of illustrating the firmness of the hold which the theory of phlogiston had over chemists some fifty years after its promulgation by Stahl, and exhibiting the ingenious, but futile, plans for fitting the theory to facts, and facts to theory, which could be devised by a man of quick wits and great flexibility of mind.

Before considering some of the work of Priestley, it is advisable, I think, to make a short digression into the history of the investigations of gaseous substances previous to the time of that ingenious and versatile man.

That the ancients recognized the existence of aeriform bodies is shown by their employment of such terms as *spiritus*, *flatus*, *halitus*, *aura*, and *emanatio nubila*. Throughout the earlier centuries of our era, references are made by various writers to the resistance of the air, the disengagement of aeriform substances by heating other substances, irrespirable airs, inflammable airs, and the like. In the first quarter of the seventeenth century a Dutch alchemist, named Drebbel, pictured an apparatus not unlike the pneumatic trough used by Priestley. In 1727 Hales described and figured a method of collecting gases which was essentially the same as that used thirty or forty years later by Black and by Priestley.

So far as we know, the word *gas* was employed first by Van-Helmont. This great naturalist was born at Brussels in

1577 and died in 1644. His works were collected after his death by his son and published in 1648.[1]

"Charcoal," said Van-Helmont, "and, in general, bodies which are not immediately resolved into water, necessarily disengage (when purest), *spiritum sylvestrem.* Sixty-two pounds of oak charcoal yield one pound of cinders. Therefore the rest, amounting to sixty-one pounds, is this *spiritus sylvestris.*[2] This spirit, hitherto unknown, which can neither be contained in vessels nor reduced to a visible body, I call by a new name, *gas (hunc spiritum incognitum hactenus, novo nomine* gas *voco).* There are bodies which enclose that spirit, and can be resolved almost wholly into it; therein it is as fixed or solidified, from which state it may be driven forth, as is seen in the fermentation of wine, bread, etc."

In another place he speaks of this gas being produced in the fermentation of grapes, apples, honey, etc.: "*Gas si multa vi intra cados coerceatur, vina furiosa reddit.*" Besides burning charcoal and fermentation, Van-Helmont mentions four other sources of *gas sylvestre:* the action of an acid on calcareous bodies; caverns, mines, and cellars; mineral waters; and the intestines during putrefaction. The expression *gas sylvestre* was used by Van-Helmont as a general term: he recognized various kinds of gases; a gas produced by mixing an acid with common salt, another by burning sulphur, and another by treating silver with *aqua fortis,* etc. It is, however, not likely that he collected and minutely examined these gases, because he says that a gas cannot be imprisoned in any vessel, and that it dashes aside all obstacles which would prevent it from mixing with the surrounding air.

The work of Boyle on the pressure of the air, culminating in the nearly complete description of the relation between the volume of air and the pressure to which the air is subjected, which is now known as *Boyle's law*, belongs rather to physics than to chemistry. Boyle recognized that air is a complicated mixture of many things; in his tract *Suspicions about some hidden Qualities in the Air*, he says:

---

[1] " *Ortus medicinæ, id est initia physica inaudita, progressus medicinæ novus in morborum ultionem ad vitam longam, edente auctoris filio.*" I have taken my account of Van-Helmont's work on gases from Hoefer (Histoire, vol. ii. pp. 135–146).

[2] Van-Helmont used this name because he thought of the new substance as untamable: " *Gas sylvestre sive incoercibile, quod in corpus cogi nonpotest visibile.*"

"For [atmospherical air] is not, as many imagine, a simple and elementary body, but a confused aggregate of effluviums from such differing bodies, that, though they all agree in constituting, by their minuteness and various motions, one great mass of fluid matter, yet perhaps there is scarce a more heterogeneous body in the world."

Some of the experiments described by Boyle, especially in *The Second continuation of physico-mechanical Experiments* and *The General History of the Air designed and begun*, show that he had prepared gases which contained the substances we now call carbon dioxide and hydrogen, and probably also hydrogen chloride, and one or more of the oxides of nitrogen, without certainly distinguishing these gases from ordinary air. Mayow (1645–1679) obtained an air by the action of diluted *spirit of nitre* on iron, which he tells us he could not believe was really ordinary air. Hales (1677–1761) prepared a number of gases, but he did not clearly distinguish any of them from atmospheric air; he seems to have been annoyed at the complexity of the atmosphere, as he abandoned the attempt to distinguish its ingredients, remarking that it was a "volatile Proteus" and a "Chaos."

About the middle of the eighteenth century, Black isolated the gas now called carbon dioxide, proved it to be a substance different from common air, examined its properties, and made a quantitative study of the part played by this gas in the changes from chalk to burnt lime, and from *magnesia alba* to magnesia.

That flame is supported by a peculiar kind of air seems to have been surmised in the early centuries of our era. This guess was strengthened by observations made during the Middle Ages, and the fact was gradually established that a combustible body generally weighs less than the product of its combustion. A comparison of the following quotations will show how slowly definite knowledge was gained concerning the changes that occur during combustion; the first quotation is from Clement of Alexandria, who flourished in the end of the second and the early part of the third century A.D., and the second is from Boyle's tract entitled *Suspicions about some hidden Qualities in the Air*, published in the last quarter of the seventeenth century,

"Airs are divided into two categories: an air for the divine flame,

which is the soul; and a material air ($\sigma\omega\mu\alpha\tau\iota\kappa\grave{o}\nu$ $\pi\nu\epsilon\hat{v}\mu\alpha$), which is the nourisher of sensible fire and the basis of combustible matter ($\tau\grave{o}\nu$ $\grave{\alpha}\iota\sigma\theta\eta\tau o\nu$ $\pi\nu\rho\grave{o}s$ $\tau\rho\sigma\phi\grave{\eta}$ $\kappa\alpha\grave{\iota}$ $\grave{v}\pi\acute{\epsilon}\kappa\kappa\alpha\nu\mu\alpha$ $\gamma\acute{\iota}\nu\epsilon\tau\alpha\iota$)." [1]

"The difficulty we find of keeping flame and fire alive, though but for a little time, without air, makes me sometimes prone to suspect, that there may be dispersed through the rest of the atmosphere some odd substance, either of a solar, or some other exotic nature, on whose account the air is so necessary to the subsistence of flame."

A book was published in 1630 by Jean Rey,[2] a French physician, who busied himself in his leisure time with physics and chemistry. Rey assigned the increase in weight which happened when tin and lead were burnt to the attachment of the particles of the air to the calces of the metals; he recognized that there was a limit to this gain in weight, that after tin or lead had been heated for some time no change of weight occurred.

" The condensed air attaches itself to the (metallic) calx, and adheres little by little to the smallest of its particles; thus, its weight increases from the beginning to the end. But when all is saturated, it can take up no more. Do not continue your calcination in this hope; you would lose your labour."

Boyle supposed that the increase in weight which occurs when a body is burnt was caused by the fixation of the particles of fire by the burning body. In *New experiments to make Fire and Flame Stable and Ponderable*, he says:

"For, supposing . . . that flame may act upon some bodies as a menstruum, it seems no way incredible, that as almost all other menstruums, so flame should have some of its own particles united with those of the bodies exposed to its action; and the generality of those particles being . . . either saline, or of some such piercing and terrestrial nature, it is no wonder, that being wedged into the pores, or being brought to adhere very fast to the little parts of the bodies exposed to their action, the accession of so many little bodies, that want not gravity, should, because of their multitude, be considerable upon a balance, whereon one or two, or but a few of these corpuscles, would have no visible effect." Boyle was careful to add, "There is a large field opened for the speculative to apply this discovery to divers phenomena of nature and chemistry."

A very remarkable work was published in 1674 by John

[1] *Sententiæ Theodoti:* quoted by Hoefer (*Histoire*, vol. I. p. 182, note)
[2] " *Essays de Jean Rey, docteur en medecine, sur la Recherche de la cause pour laquelle l'Estain et le Plomb augmentent de poids quand on les calcine*, Bazas, 1630. (A translation of Rey's Essay is published as No. 11 of the *Alembic Club Reprints.*)

Mayow,[1] wherein the statement was made very clearly, and was supported by experiments, that the atmosphere contains two kinds of aërial particles; that the more active particles (*spiritus nitro-ærus*) support combustion and the respiration of animals, and the other particles (*spiritus nitri acidi*) are corrosive and extinguish fire. Mayow said that the fire-nourishing air constituted only a part, the most active part, of the atmosphere:

> "At non est existimandum pabulum igno-aereum ipsum aerem esse, sed tantum ejus partem magis activam."

This same fiery air was declared by Mayow to exist in nitre; for, he stated, that as a mixture of nitre and sulphur can be inflamed in a jar emptied of air, the particles that nourish flame must be supplied by the nitre. To the question, What comes of the particles of the fiery air during combustion? Mayow said he did not know, but perhaps they were changed into another harmful air. He compared the *diaphoretic antimony* produced by burning antimony by the sun's rays, concentrated by a lens, with the substance formed by the action of the acid of nitre on antimony. These substances, said Mayow, are exactly alike; there is a similar increase in weight in both processes, and this increase is almost constant. This increase can scarcely be thought of, Mayow remarked, as due to any other cause than the fixation of the particles of nitre-air during calcination:

> "Quippe vix concipi potest unde augmentum illud antimonii nisi a particulis nitro-aereis igneisque ei inter calcinandum infixis procedat."

Mayow opposed the view that sulphur contains a principle which changes it into an acid when it is burnt; he said that the acid formed by burning sulphur is the result of the laying hold of the particles of nitre-air by the sulphur, and that an acid is formed by heating sulphur with spirit of nitre which, in all respects, is like the acid formed by distilling vitriol. Mayow showed, experimentally, that the nitre-air in the atmosphere is necessary for the respiration of animals. He measured the

---

[1] *Tractatus quinque medico-physici, quorum primus agit de sale nitro et spiritu nitro-aereo; secundus de respiratione,* etc., *Studio,* Joh. Mayow. Oxonii, 1674.

air left in a jar, standing over water, wherein a mouse had lived until the water ceased to rise in the jar, and he found that the original air had decreased by about one fourteenth of its volume. Although he thought that the elasticity (that is, resistance to compression) of air was due to the particles of fiery air, or nitre-air, in it, yet he admitted that his experiments showed that the air which remained when a body was burnt, or an animal breathed, in an enclosed volume of air, was as elastic as ordinary air.   He could not explain this difficulty: the air which remained in a vessel after the particles of nitre-air had been removed by a burning body ought to be less elastic than common air; nevertheless, this residual air was not less elastic than common air, although something (to which the elasticity of air is due, according to Mayow) had been removed from the common air.

Mayow, of course, tried to restore to air what it loses by combustions or respirations proceeding in it.   He filled a small bottle with a mixture of equal parts of spirit of nitre and water, threw some little pieces of iron into this bottle, and inverted it in another vessel containing the same liquid as was in the bottle.   He noticed a gas (*halitus*) rise in the liquid and collect in the upper part of the bottle; he said that this gas (*aura*) could not be condensed to a liquid however much it was cooled. He then used oil of vitriol and water in place of spirit of nitre, and by acting on iron with this mixture he obtained a gas which, he said, was the same as that produced when spirit of nitre was used.   To the question, Is this aeriform substance true air? Mayow replied that it had the same appearance and the same elasticity as common air, and it contracted by cold; but, in spite of that, he said he could scarcely believe that it was indeed ordinary air.

Boyle, also, obtained a gas by acting on iron with diluted oil of vitriol; he called this gas "air generated *de novo*," and he thought it possible that particles of water, or other substances, might be so agitated as to merit the name *air*.

At the end of the seventeenth century no definite answer had been given to the question, What happens when a substance is burnt in air?   The experiments of several naturalists had made it very probable that particles of a particular kind of air

were absorbed by the burning substance; if this were so, the air that remained must be different from common air; but it should be possible to get again from the burnt substance the peculiar fiery air (or nitre-air, or vital air) it had absorbed, and, by mixing this with the air that remained unconsumed, to re-form common air. Chemistry had to wait about three-quarters of a century before this possibility was realized. The theory of phlogiston arose early in the eighteenth century, and set men on the wrong track by giving what seemed to be, and at the time certainly was, a simple and satisfactory description of most of the qualitative facts concerning combustion. Until processes of burning had been examined more exhaustively and more rigorously, the phlogistic conception served as a convenient and generally applicable means of expressing facts. That theory, moreover, suggested new lines of investigation, and many very able and productive chemists adopted it as a guide. It was the attempt to find an interpretation of facts brought to light by ardent phlogisteans that led to the abandonment of the theory of phlogiston.

I have already given some account of that theory. That we may realize how pliable the theory was in the hands of a man of nimble mind and restless curiosity, and how entirely it could dominate the chemical conceptions of a man of keen intellect, let us consider some of the work of Priestley on subjects connected with combustion.

Joseph Priestley (1733–1804) was the first experimenter to prepare many different gaseous substances; his experiments, which were numerous and varied, showed that some of these substances contained airs, or gases, different from common air and from one another. But, so far as I am able to judge, after reading his six volumes entitled *Experiments and Observations on different kinds of Air*, he separated very few, if any, homogeneous gaseous substances from the mixtures of gases which were produced in his experiments. By acting on iron, zinc, and tin with diluted acids, Priestley obtained "inflammable air"; and he produced what he took to be the same air by heating all manner of animal, vegetable, and combustible mineral matters in gun-barrels. "Noxious air" he got by causing animals to

live in confined volumes of common air, by allowing vegetables
to decay in air, by heating beef, mutton, etc., and by other
methods. He made "nitrous air" by the action of *spirit of
nitre* on iron, copper, tin, and some other metals, and by the
action of *aqua regia* on gold and the "regulus of antimony."
By the action of *spirit of salt* on various metals, Priestley pre-
pared "marine acid air;" and "vitriolic acid air" he made by
heating oil of vitriol with olive oil or with metals. He also
prepared "alkaline air," "vegetable acid air," and many other
airs. Priestley's most famous experiment on the production
of a new kind of air was that which he performed in 1774. He
says: [1]

"Having procured a lens of twelve inches diameter, and twenty inches
focal distance, I proceeded with great alacrity to examine, by the help of it,
what kind of air a great variety of substances, natural and factitious, would
yield. . . . With this apparatus, after a variety of other experiments, an
account of which will be found in its proper place, on the 1st of August,
1774, I endeavoured to extract air from *mercurius calcinatus per se;* and I
presently found that, by means of this lens, air was expelled from it very
readily. Having got about three or four times as much as the bulk of my
materials, I admitted water to it, and found that it was not imbibed by it.
But what surprized me more than I can well express, was, that a candle
burned in this air with a remarkably vigorous flame, very much like that
enlarged flame with which a candle burns in nitrous air, exposed to iron
or liver of sulphur; but as I had got nothing like this remarkable appearance
from any kind of air besides this particular modification of nitrous air, and
I knew no nitrous acid was used in the preparation of *mercurius calcinatus*, I
was utterly at a loss how to account for it. . . . At the same time that I
made the above-mentioned experiment, I extracted a quantity of air, with
the very same property, from the common *red precipitate*, which being pro-
duced by a solution of mercury in spirit of nitre, made me conclude that
this peculiar property, being similar to that of the modification of nitrous
air above-mentioned, depended upon something being communicated to it by
the nitrous acid; and since the *mercurius calcinatus* is produced by exposing
mercury to a certain degree of heat, where common air has access to it, I
likewise concluded that this substance had collected something of *nitre*, in
that state of heat, from the atmosphere."

Priestley thought that the *mercurius calcinatus* he had used
might have been "nothing more than red precipitate," inas-
much as it was "bought at a common apothecary's"; he was
therefore very careful to obtain a specimen of *mercurius cal-*

cinatus "of the genuineness of which there could not possibly be any suspicion." This yielded the same kind of air as his other specimen.

"But what I observed new at this time (Nov. 19), and which surprized me no less than the fact I had discovered before, was, that, whereas a few moments agitation in water will deprive the modified nitrous air of its property of admitting a candle to burn in it; yet, after more than ten times as much agitation as would be sufficient to produce this alteration in the nitrous air, no sensible change was produced in this." (*L. c.*, p. 39.)

He allowed the specimen of the new air to stand over water for two days, and then agitated it violently with water; and he was more surprised than ever to find that a candle still burnt in it. He was surprised, because he thought the new air was much the same thing as "nitrous air" that had stood over iron and liver of sulphur; but his former experiments had taught him that "nitrous air" thus treated, and then agitated with water, would not have supported the burning of a candle. About four months later (March, 1775), Priestley began to suspect that his new air was fit for respiration. He had been accustomed for two or three years to test the "goodness" of common air by shaking it with "nitrous air" over water and noticing the diminution of volume that occurred. In March, 1775, he applied "this test of nitrous air" to the air from *mercurius calcinatus*, and he found that the new air behaved like common air. He set aside the mixture he had made of nitrous air and the air from *mercurius calcinatus* over water; the next day he was "more surprised than ever he had been before" to find that a candle still burned in this air. The remark which Priestley makes at this point is very characteristic:

"I cannot, at this distance of time, recollect what it was that I had in view in making this experiment. . . . If, however, I had not happened, for some other purpose, to have had a lighted candle before me, I should probably never have made the trial; and the whole train of my future experiments relating to this kind of air might have been prevented."

Priestley now began to think that his new air was "at least as good as common air"; the fact that a full-grown mouse lived in this air for half an hour, whereas such a mouse usually lived for only a quarter of an hour in a confined quantity of common

air, confirmed this opinion.   After reflecting on the behaviour of
the mouse, he says it gave him "so much suspicion that the air
into which [he] had put it was better than common air," that
he applied the nitrous test to a portion of the air wherein the
mouse had breathed for half an hour; instead of finding this
air "noxious," as common air would have been after a mouse
had lived in it even for quarter of an hour, he found that it was
"better" than common air, as he measured betterness by the
"nitrous air test."   Reducing the volume of common air by
adding nitrous air to it over water was called by Priestley a
"phlogistic process": he says he had not found any phlogistic
process so much diminish common air as the nitrous air test
diminished his new air after a mouse had breathed in it for half
an hour.   Priestley lay awake that night in "utter astonish-
ment."   Next day he popped the same mouse into what re-
mained of the air wherein it had been confined for half an hour
the day before; the mouse now "remained perfectly at its ease
another full half hour, when I took it out, quite lively and
vigorous."

At last Priestley recognized that his new air was "of a
superior goodness" to common air, and he proceeded to measure
"that degree of purity . . . by the test of nitrous air."   The
result was that "two measures of this air took more than two
measures of nitrous air, and yet remained less than half of what
it was."   He had already found that two measures of common
air took about one measure of nitrous air, and that "the whole
was reduced to one fifth less than the original quantity of
common air."   From these results Priestley concluded that the
new air "was between four and five times as good as common
air"; he adds, "I have since procured air better than this,
even between five and six times as good as the best common air
that I have ever met with." [At a later time he obtained al-
most pure dephlogisticated air (see *Continuation of Observa-
tions on Air*, vol. i. p. 246).]   Priestley regarded nitrous air
as the *fumes of spirit of nitre* combined with phlogiston; he
thought of air "as wholesome in proportion to the quantity of
phlogiston that it is able to take" from other substances.
When wholesome air was shaken with nitrous air over water,

Priestley said that the phlogiston left the nitrous air and united with the common air, and that the red air which was seen was the *fumes of spirit of nitre*, that is, nitrous air deprived of its superabundant phlogiston. As his new air required more nitrous air for its saturation than an equal volume of common air required, the new air was evidently able to take more phlogiston from nitrous air than common air could take; hence the new air was more dephlogisticated than common air. Priestley thought of the differences between airs as differences of qualities which could be put off or on by suitable processes. The new air was to him only common air in a state of greater purity than usual. He was anxious to find how it was that common air had become so pure, or, in his language, so dephlogisticated. He therefore "proceeded to examine all the preparations of lead made by heat in the open air, to see what kind of air they would yield." Red lead, litharge, and various other preparations of lead yielded more or less pure air when heated by help of the lens: a specimen of freshly made red lead gave him very little air, but this air was very pure; he thought he might be able "to bring this fresh made red lead, which yielded very little air, to that state in which other red lead had yielded a considerable quantity." Priestley supposed "that red lead must imbibe from the atmosphere some kind of acid, in order to acquire" the property of yielding dephlogisticated air when heated; he therefore moistened portions of his red lead "with each of the three mineral acids, viz., the vitriolic, the marine, and the nitrous," dried the mixtures, and heated them in gun-barrels. The "composition into which the nitrous acid had entered" was the only one that gave air; much of this was fixed air, according to Priestley's experiments, but some of it was dephlogisticated air. When he moistened some of his red lead with less of *the spirit of nitre* than before, dried and heated the mixture, he got "not quite a pint of air; but it was almost all of the dephlogisticated kind, about five times as pure as common air." He was now convinced "that it was the nitrous acid which the red lead had acquired from the air, and which had enabled it to yield the dephlogisticated air." This conviction was strengthened by other experiments wherein he

moistened various earths [1] with *the spirit of nitre,* and heated the mixtures in gun-barrels; in each case he obtained dephlogisticated air. Priestley was now satisfied that his new air was pure air, or, in his language, dephlogisticated air; and, as regards the atmosphere, he says:

"There remained no doubt in my mind but that *atmospherical* air, or the thing we breathe, *consists of the nitrous* acid and *earth,* with so much phlogiston as is necessary to its elasticity, and likewise so much more as is required to bring it from its state of perfect purity to the mean condition in which we find it."

The name *dephlogisticated air* embodied accurately Priestley's conception of the relation of this air to atmospheric air. The latter was supposed by him to contain sufficient phlogiston not only to keep its component parts, "the nitrous acid and earth," in the state of an elastic fluid, but also to temper its purity to such a degree as to make it suited for the performance of its various functions; the removal of the superabundant phlogiston was the formation of the new air; the new air was nothing more than a purer form of atmospheric air.[2] To dephlogisticate an air meant, in Priestley's language, to purify that air; he said, "phlogistic matter is the very bane of purity with respect to air, they being exactly *plus* and *minus* to each other."

Priestley thought of the atmosphere as being constantly "vitiated" or "rendered noxious," or "depraved" or "corrupted," by processes of respiration, combustion, and the like; and he showed that air which has been rendered noxious is "depurated" by the combined action of green plants, water, and sunlight upon it.

It is not easy to form a clear picture of the process which was supposed by Priestley to occur when atmospheric air was dephlogisticated by first heating lead in it, and then more strongly heating the red lead that was formed. "Metals," said Priestley, "are generally supposed to consist of nothing

---

[1] " For this purpose I tried, with success, *flowers of zinc, chalk, quicklime, slacked lime, tobacco-pipe clay, flint,* and *Muscovy talck,* with other similar substances." (*Experiments on Air,* 2d Ed., vol. ii. p. 55.)

[2] In one place he speaks of atmospheric air as being the same thing as dephlogisticated air, " but in a state of inferior purity "; and in another place he says of atmospheric air that it is " only dephlogisticated air in a state of depravation."

but a metallic earth united to phlogiston." When a metal was calcined it was supposed to lose phlogiston: but more than that occurred; Priestley noticed that the calcination was accompanied by a diminution of the air wherein the metal was heated; he accounted for that diminution by supposing, first, that there was "some particular mode of combination, or degree of affinity with which we are not acquainted," between the phlogiston set loose from the metal and the air which received that phlogiston; and, secondly, that (in some cases at any rate) the metal imbibed something from the air. As regards lead, Priestley supposed that red lead "must get the property of yielding this kind of air [1] [that is, dephlogisticated air] from the atmosphere"; and at one time he concluded "that it was the nitrous acid which the red lead acquired from the air, and which enabled it to yield the dephlogisticated air." [2] Putting together the views expressed by Priestley, I think we may conclude that he regarded the calcination of lead as a process wherein phlogiston was taken away from the metal, and, at the same time, the metallic earth that remained imbibed something, probably the nitrous acid, from the atmosphere; that he looked on the process as a change from a union of a metallic earth with phlogiston to a union of that earth with something which was probably the nitrous acid (a little phlogiston, I suppose, being left); and that he thought of the process that occurred when red lead was heated strongly as the escape of an air, which consisted of an earth united to the nitrous acid and enough phlogiston to maintain the whole as an elastic fluid.[3] The "modes of union" of the earth with phlogiston, and the nitrous acid with phlogiston, in atmospheric air, were supposed by Priestley to be different

---

[1] This expression, " must get the property of yielding this kind of air," is characteristic of Priestley's view of chemical changes; the expression is essentially alchemical.

[2] In 1786 (*Continuation of Observations on Air*, iii. p. 420), Priestley admitted the justness of Lavoisier's conclusions, from his experiments, that mercury heated " in contact with pure air, or with anything that contains pure air, imbibes, indeed, the pure air, and nothing else."

[3] From remarks in vol. iii. of *Experiments and Observations on Air* (pp. 21, 36), and in vol. i. of *Continuation of the Observations on Air* (p. 198), it would seem as if Priestley, in 1779, thought that, when he added " the nitrous acid " to a solid and obtained an air by heating the mixture, he converted the solid itself into an air.

from the "mode of union" of the earth with phlogiston in the metal.[1]

I suppose it is possible to say that, a few years after he obtained dephlogisticated air, Priestley thought of the production of that air by heating red lead which had been formed by calcining lead in air, in a vague and nebulous way, as the taking of something out of the air by the hot lead, and the obtaining of some kind of modification of that something from the red lead.

Priestley was a staunch adherent of the phlogistic theory; he stated all his conclusions, and many of his facts, in the language of that theory; but he also widened and modified the conception of phlogiston in such a way that it lost more in clearness than it gained in comprehensiveness.

"Nothing can burn," said Priestley, "unless there be something at hand to receive the phlogiston which is set loose in the act of ignition." He did not consider it absolutely necessary that air should be the recipient of the phlogiston set loose in processes of combustion; the phlogiston might perhaps be communicated to water or to other substances. When he spoke of air, or sometimes dephlogisticated air, as the *pabulum* of a burning body, Priestley meant that the air received the phlogiston which was "set loose in the dissolution" of the burning body. Airs were regarded by Priestley as unions of phlogiston with different bases, and he recognized different modes of union: thus, he speaks of "that mode of union [of phlogiston] with its base which constitutes inflammable air," and of another mode of union as "that which constitutes an air that extinguishes flame." The modes of union could be changed by such a process as shaking the airs with water: Priestley said he had "indisputable evidence that inflammable air, standing long in water, has actually lost all its inflammability, and even come to extinguish flame much more than that air in which candles have burned out."

---

[1] Priestley's view of the nature of dephlogisticated air became more complicated and confused as his experiments proceeded; but in the last of his six volumes on *Air* (1786) he was inclined to follow Lavoisier in regarding this air as an elementary substance.

Priestley gave an ingenious statement in terms of his phlogistic hypothesis of the fact that ordinary air is reduced in volume by calcining a metal in it and the air which remains is not inflammable. If, as was asserted, phlogiston escapes into the air when a metal is calcined, one would suppose that the volume of air would be increased by the amount of phlogiston released from the metal; and if, as was also asserted, phlogiston is the principle of inflammability, one would suppose that air loaded with this principle would be inflammable.[1] The phlogiston released from the metal, Priestley said, combines with the air that receives it in such a way that the volume of this union is less than the volume of the air without the phlogiston; and the mode of union of the air and phlogiston is of that kind which constitutes a non-inflammable air. If saturating ordinary air with phlogiston diminished the air, then, as shaking noxious air (that is, air loaded with phlogiston) with water was said to extract phlogiston therefrom, it might be supposed, Priestley remarks, that this extraction of phlogiston from noxious air would increase the volume of the air. But the "restoration" of noxious air by shaking with water did not increase the volume of the air. The reason was at hand—because some phlogiston remains in the air, and the mode of union of the phlogiston with the air is so changed that the volume of the combination is not greater than that of the other combination which was present before the process of "restoration" began.

When Lavoisier had proved that the change which occurs when mercury is calcined in the air consists in the absorption, by the mercury, of dephlogisticated air from the atmosphere, and that mercury and dephlogisticated air are the only things formed when the calx of mercury is decomposed by heat, there seemed to be no part left for phlogiston to play in this cycle of changes. The ingenious Priestley rose to the occasion. He admitted that the heated mercury imbibed "pure air, and nothing else"; but, following Kirwan, he said:

"The phlogiston belonging to the metal unites with that air so as together

---

[1] In one place (*Continuation of the Observations on Air,* ii. p. 218) Priestley states that "alkaline air, indeed, contains phlogiston, because ... it is itself partfally inflammable."

to form *fixed air*,[1] and therefore the calx may be said to be the metal united to fixed air. Then, in a greater degree of heat than that in which the union was formed, this factitious fixed air is again decomposed; the phlogiston in it reviving the metal, while the pure air is set loose. Consequently the precipitate actually contains within itself all the phlogiston that is necessary to the revival of the mercury." Priestly adds: "Since, therefore, this fact *can* be accounted for without excluding phlogiston, the supposition of which is exceedingly convenient, if not absolutely necessary, to the explanation of many other facts in chemistry, it is at least advisable not to abandon it."[2]

Priestley was of opinion, in 1779, that iron would rust in very pure dephlogisticated air, because that air ought to draw the phlogiston out of the iron, and the metallic earth (rust) would then be seen. He found that about one tenth of the dephlogisticated air in which he exposed clean iron nails disappeared after nine months; although he could not see any rust, he concluded that his conjecture was well-founded; at any rate he was convinced that the pure air had been diminished by the phlogiston from the iron (*Continuation of Observations on Air*, vol. i. p. 253).

The protean principle of phlogiston was always at Priestley's elbow, ready for any emergency. He supposed that nothing conducts electricity which does not contain phlogiston, that nothing nourishes animals which does not contain phlogiston, and that the source of muscular action is phlogiston.[3]

He conjectured that animals are able to convert phlogiston "from the state in which they receive it in their nutriment, into that state in which it is called the electrical fluid;" and that the nerves can direct "this great principle thus exalted," by the brain, into the muscles which are thereby forced to act.

---

[1] This statement, of course, assumes that *fixed air* was a " mode of union " of phlogiston and pure (or dephlogisticated) air. Neither fixed air nor any other air was regarded by Priestley as a definite substance having a definite and unchangeable composition.

[2] *Continuation of Observations on Air*, vol. iii. pp. 420–21 (1786).

[3] " That the source of muscular motion is phlogiston is still more probable, from the consideration of the well-known effects of vinous and spirituous liquors, which consist very much of phlogiston, and which instantly brace and strengthen the whole nervous and muscular system; the phlogiston in this case being, perhaps, more easily extricated, and by a less tedious animal process, than in the usual manner of extracting it from mild aliments. Since, however, the mildest aliments do the same thing more slowly and permanently that spirituous liquors do suddenly and transiently, it seems probable that their operation is ultimately the same." (*Experiments and Observations on Air*, vol. i. pp. 276–77.)

He also said "it is probable that all light is a modification of phlogiston."

With such an accommodating and tractable hypothesis as phlogiston always at hand, Priestley did not feel the need of accurate quantitative experiments. His work did not demand a careful examination of the materials he employed to produce substances that had a superficial resemblance to one another. He was not compelled, as Boyle had been a hundred years before him, to attribute differences in the results of experiments performed under what seemed the same conditions to small, overlooked differences in these conditions. That most pliant principle of phlogiston which guided him saved him the trouble of trying to form clear conceptions of chemical action and chemical composition. Priestley did not picture to himself chemical change as an orderly process occurring between definite substances, each of which had distinct properties. He did not accurately weigh the materials he used and the products he obtained; he did not attempt to account for everything that took part in the transformations he examined. He dealt in principles, qualities, modes of union, and superficial resemblances and differences. His "philosophical pursuits," he tells us, "were only occasional." Priestley was an alchemist, not a chemist. Nevertheless his experiments, which were numerous, varied, and very suggestive, did much to advance the study of chemical change; some of his results passed away, many formed the foundations of investigations which were of supreme importance to chemistry.

Scheele (1742–1786) and Cavendish (1731–1810) did much towards the recognition of chemical processes as ordered changes occurring between distinct kinds of substances; their experimental work greatly advanced the methods by which the two fundamental inquiries of chemistry might be pursued, and were also of much direct help in furthering these inquiries.

I shall give short accounts of those parts of the work of these two naturalists which deal with the chemical study of the air.

Carl Wilhelm Scheele earned his living as an apothecary in Malmö, Upsala, and some other towns of Sweden. Every spare moment he devoted to chemical experiments; the real interests

of his life were those of the laboratory.   In 1777 was published his *Chemische Abhandlung von der Luft und dem Feuer*.[1]

Scheele enumerates certain properties which he regarded as characteristic of common air, then he says:

"When I have a fluid resembling air . . . and find that it has not the properties mentioned, even when only one of them is wanting, I feel convinced that it is not ordinary air."

He exposed air, in bottles of known capacity, to the action of such substances as "alkaline liver of sulphur," oil of turpentine, the precipitate produced by adding caustic ley to a solution of "the vitriol of iron," moist iron-filings, phosphorus, etc.; he also burnt phosphorus in an enclosed volume of air, and then opened the vessel under water; and he burned a candle, and also inflammable gas (obtained by acting on iron, zinc, or tin with diluted oil of vitriol or marine acid), in air over water.   By measuring the volumes of water which rushed into the vessels wherein the processes were conducted, Scheele determined what fraction of the original volume of air had disappeared in each experiment.   He also examined the air that remained, and, finding it would not support combustion, he called it *vitiated air*.

The conclusions which he drew from the results of these experiments are stated by Scheele as follows:

"Thus much I see from the experiments mentioned, that the air consists of two fluids, differing from each other, the one of which does not manifest in the least the property of attracting phlogiston, while the other, which composes between the third and the fourth part of the whole mass of the air, is peculiarly disposed to such attraction.   But where this latter kind of air has gone to after it has united with the inflammable substance, is a question which must be decided by further experiments, and not by conjectures."

In his "further experiments," Scheele endeavoured to obtain an air which would behave towards phosphorus, liver of sulphur, oil of turpentine, etc., in the same way as that part of common air which he said was peculiarly disposed to attract phlogiston from inflammable bodies.   By distilling nitre with oil of vitriol

---

[1] A translation of those parts of this treatise which bear on the composition of the atmosphere and the phenomena of combustion has been published as No. 8 of the *Alembic Club Reprints* (Wm. F. Clay, Edinburgh, 1894).   The quotations in the text are from that translation.   Many of Scheele's letters, and extracts from his laboratory note-books, were published in 1892 by A. E. Nordenskiöld, with the title, *Carl Wilhelm Scheele, Nachgelassene Briefe und Aufzeichnungen* " [Stockholm, P.A. Norstedt & Söner].

and heating until the apparatus was filled with red vapour, he obtained an air wherein a candle burned very briskly and brightly: this he called *fire-air*. He obtained this fire-air from various substances and by different methods; for instance, by heating oil of vitriol with finely powdered "*manganese*," by evaporating to dryness a solution of magnesia in *aqua fortis* and strongly heating the residue, by distilling "*mercurial nitre*," by heating nitre, and by heating the calx of silver, the calx of gold, and red precipitate. He found that this fire-air was absorbed by those substances which, he had before shown, caused to disappear a portion of the common air wherein they had been burnt, or exposed for some time. Then he says:

"These experiments, show, therefore, that this fire-air is just that air by means of which fire burns in common air; only it is there mixed with a kind of air which seems to possess no attraction at all for the inflammable substance, and this it is which places some hindrance in the way of the otherwise rapid and violent inflammation."

Scheele's *Laboratory Notes* show that he had obtained fire-air (it is called *aer vitriolicus* in the earlier notes) in 1771, by heating *mercurius calcinatus*, "*mercurius præcipit. ruber*," "*sol. argenti in acido nitri*, mit *alkali fixo crystallisirto* praecipitirt," and by several other methods.[1]

Scheele does not seem to have regarded his experimental results as proving, conclusively, that fire-air is absorbed by a body burning therein, or in common air. One might suppose that the diminution observed in the volume of the air wherein phosphorus or inflammable gas, etc., was burned, and the fact that the air which remained was "vitiated air," would compel the conclusion that the burning body had absorbed something from the air. But Scheele, like Priestley, supposed that the phlogiston drawn out of the combustible substance by the fire-air in the atmosphere diminished the volume and altered the properties of the residual air.

---

[1] It is interesting to notice that, in 1489, Eck de Sulzbach proved that the calx of mercury, obtained by heating mercury in the air for many days, weighed more than the mercury before it was heated; and that he said " this increase in weight is caused by the union of a spirit with the body of the metal; and what proves this is, that artificial cinnabar [one of the names given by him to the calx of mercury] disengages a spirit when it is submitted to distillation." (Quoted by Hoefer, *Histoire de la Chimie*, vol. i. p. 472.)

In a letter to Bergmann, in November, 1781,[1] Scheele wrote as follows:

"That red lead and calamine give *pure air*, I well believe; but I still much doubt that this air was bound to the calx before it was evolved; but should it be so, then this *pure air* is bound to the metallic phlogiston, and is present in the calx as *materia caloris*, for this calx and other metallic calces prepared in the fire, and also *mercurius calcinatus per se*, are able to attract the *pure air* by help of their phlogiston, to lose their lustre, and to be changed to calx. . . . If the phlogiston has weight, then the *pure air* obtained in the reduction is derived from the heat imprisoned in the metallic earths, because metals increase in weight when calcined by as much as is the quantity of pure air that is combined with them. . . . We know that our atmospheric air certainly decomposes burning sulphur, but vitriolic acid does not rob it of quite the whole of its phlogiston; hence the volatile sulphuric acid. Now, at the end of a process of distillation, iron vitriol smells of volatile sulphuric acid, hence, very concentrated *acidum vitrioli* is able to decompose this heat, at a red heat, and hence comes the *pure air*."

At the end of this letter, Scheele said:

"It is very possible that my opinions are quite erroneous; nevertheless, time will make all clear."

In the latter part of his treatise on *Air and Fire*, Scheele describes various experiments on the action of living animals on fire-air.   He also breathed that air himself, then exhaled, and collected and examined his expired breath.   He concluded that living animals change fire-air into aërial acid (that is, into what is now called carbon dioxide).

"I am inclined to believe," he says, "that fire-air consists of a subtle acid substance united with phlogiston, and it is probable that all acids derive their origin from fire-air."[12]

Scheele also found that fire-air was absorbed by water, and he

[1] *Briefe und Aufzeichnungen*, pp. 340–342.   (This letter was written in German.)

[2] The opinions held by Scheele, in 1775, regarding fire-air, inflammable air, heat, light, and combustion are expressed in a letter of his to Gahn (written in Swedish) [*Briefe und Aufzeichnungen*, pp. 79, 80]: " Heat consists of fire-air combined with phlogiston.   It passes through glass and all vessels . . . . Light consists of fire-air and more phlogiston than heat . . . . Inflammable air consists of fire-air and yet more phlogiston than light.   It contains so much phlogiston that it is thereby rendered inactive. . . *Combustion*.   In this process it is first necessary that another body, as heat or electricity, should separate and expand, to a certain degree, the particles of the material to be burnt.   When this has happened, the attraction between the *partes constitutivas* of the material is no longer so strong, and finally, the affinity of the phlogiston of the combustible body for the surrounding fire-air gets an opportunity to act.   The phlogiston and the fire-air combine to a new and increased heat, and the body is decomposed."   This letter shows that a great part of Scheele's experimental work on fire and air was completed before the end of the year 1775.

said that when common air was kept over water which had been boiled, the fire-air was absorbed by the water, and that the air which remained extinguished a lighted candle. His test for the presence of fire-air in water is noticeable:

"I have a convenient method to ascertain whether fire-air is present in water or not. I take, for example, an ounce of it, and add to it about 4 drops of a solution of vitriol of iron, and 2 drops of a solution of alkali of tartar which has been somewhat diluted with water. A dark green precipitate is immediately formed, which, however, becomes yellow in a couple of minutes if the water contains fire-air; but if the water has been boiled, and has become cold without access of air, or if it is even a recently distilled water, the precipitate retains its green colour, and does not become yellow sooner than an hour afterwards, and not yellow at all if it is protected from access of air in full bottles."

Besides his work on combustion and air, Scheele prepared a great number of definite chemical substances and carefully studied many of their reactions. Notable among his discoveries was that of "dephlogisticated marine acid" (now called chlorine). He obtained this gas by heating a solution of "manganese" (manganese dioxide) in marine acid (hydrochloric acid).

"What happens to the solution," he said, "is as follows: the manganese is first attracted by the marine acid, whence a brown solution arises. By the help of the acid this dissolved manganese acquires a strong attraction for phlogiston, and actually draws it to itself from the particles of acid wherewith it is united. This part of the acid, which has thus lost one of its constituents and is only very loosely united to the now more phlogisticated manganese, is driven out from its earth by the remaining marine acid which has not yet suffered any decomposition, and appears then, with effervescence, as a highly elastic air, or similar fluid."[1]

The experiments of Scheele covered an enormous field. Among other substances he prepared and examined new compounds of the alkalis, of aluminium, of ammonia, of antimony, arsenic, barium, boric acid, copper, iron, magnesium, and manganese, of molybdenum, tungsten, and platinum; his experiments helped much to make clear the chemical relations of such substances as hydrogen, nitre, silicic acid, sulphur acids, and Prussian blue; he was the first chemist to prepare acetic ether, microcosmic salt, saccharic acid, tartaric acid, and several other

---

[1] Quoted from the translation of parts of Scheele's memoir on *Manganese* (1774), published as No. 13 of the "Alembic Club Reprints." [Wm. F. Clay, Edinburgh, 1894.]

compounds. If the discovery of oxygen is to be attributed to any one chemist, it should be attributed to Scheele.

The Honourable Henry Cavendish was born in 1731 and died in 1810. In life he was passionless, and in death unmoved. His one pursuit was the investigation of physical and chemical occurrences. In that pursuit he showed great ability, determination, and accuracy. Cavendish regarded the changes that occur in processes of combustion from the position of the phlogistic theory; the conclusions he drew from his experiments were, therefore, neither decisive nor exact.

The most important work done by Cavendish on the chemistry of the air was published in two papers in the *Philosophical Transactions* for 1784 and 1785.[1] In the first paper Cavendish took up the question which Priestley and Scheele had endeavoured to answer.

"The following experiments," he said, "were made principally with a view to find out the cause of the diminution which common air is well known to suffer by all the various ways in which it is phlogisticated, and to discover what becomes of the air thus lost or condensed."

The methods of phlogisticating common air, which Cavendish selected as suitable for his purpose, were "the calcination of metals, the burning of sulphur or phosphorus, the mixture of nitrous air, and the explosion of inflammable air." The results of his experiments on exploding mixtures of inflammable air "procured from zinc" and common air showed, that when 423 measures of inflammable air are mixed with 1000 measures of common air, and the mixture is exploded by electricity, "almost all the inflammable air, and about one fifth part of the common air, lose their elasticity, and are condensed into the dew which lines the glass." He proved that the dew was "plain water," "and consequently that almost all the inflammable air, and about one fifth of the common air are turned into pure water." By exploding a mixture of dephlogisticated air, "procured from red precipitate" and inflammable air, in the proportion of 19·5 measures of the former to 37 measures of

[1] *Experiments on Air, Phil. Trans.*, **74**, 119–153, **75**, 372–384. In the first paper Cavendish says that many of the experiments therein described were made in the year 1781.

the latter, Cavendish found that "almost all of [the included air] lost its elasticity." The liquid formed by this explosion contained a noticeable quantity of "nitrous acid." He then increased the quantity of inflammable air relatively to that of dephlogisticated air, and he found that the liquid which was formed was not at all acid: he says,

"If the proportion [of inflammable air to dephlogisticated air] be such that the burnt air is almost entirely phlogisticated, the condensed liquor is not at all acid, but seems pure water, without any addition whatever; and as, when they are mixed in that proportion, very little air remains after the explosion, almost the whole being condensed, it follows, that almost the whole of the inflammable and dephlogisticated air is converted into pure water."

Cavendish thought that the small quantity of the two airs which remained unchanged to water after the explosion was due to the impurities mixed with these airs, "and, consequently," he says, "if those airs could be obtained perfectly pure, the whole would be condensed." The conclusion drawn by Cavendish from his experiments was that

"Dephlogisticated air is in reality nothing but dephlogisticated water, or water deprived of its phlogiston; or in other words, that water consists of dephlogisticated air united to phlogiston; and that inflammable air is either pure phlogiston, . . . or else water united to phlogiston; since, according to this supposition, these two substances united together form pure water."

Cavendish thought that the supposition that inflammable air is "water united to phlogiston" was much more probable than that which regarded inflammable air as pure phlogiston.

Cavendish spoke of "phlogisticated air" as appearing "to be nothing else than the nitrous acid united to phlogiston." And he said:

"The vitriolic acid, when united to a smaller proportion of phlogiston, forms the volatile sulphureous acid and vitriolic air . . . but, when united to a greater proportion of phlogiston, it forms sulphur . . . in which the phlogiston is more strongly adherent."

The substances now called nitrogen and nitric acid, on the one hand, and, on the other hand, the substances now known as sulphuric acid, sulphur dioxide, and sulphur, were thought of by Cavendish as more or less phlogisticated forms of two things. His view of the formation of water seems to have been this.

When water deprived of phlogiston is exploded with water united to phlogiston, the former attracts the phlogiston from the latter: what is required to convert dephlogisticated air (that is, water deprived of phlogiston) into water is addition of phlogiston; this necessary phlogiston is supplied by exploding dephlogisticated air with inflammable air, for the latter is water united to phlogiston. The change consists in the withdrawal of phlogiston from the inflammable air, the residue, of course, being water, and the transference of this phlogiston to the dephlogisticated air, the product, again, being water. The process was evidently thought of by Cavendish as consisting in a transference of phlogiston from one body, which had too much of that principle, to another body, which had too little of the same principle. Cavendish was inclined to regard red precipitate as a substance composed of mercury and water, "one or both of which are deprived of part of their phlogiston"; when red precipitate is decomposed by heat, he supposed that "the water in it rises deprived of its phlogiston, that is, in the form of dephlogisticated air, and at the same time the quicksilver distils over in its metallic form." Here, again, the essential change was thought of by Cavendish to be a transference of phlogiston from one body to another. Cavendish gives a very clear account of the description of the phenomena dealt with in his paper of 1784, in terms of Lavoisier's oxygen hypothesis.

"According to this hypothesis," he says, "we must suppose, that water consists of inflammable air united to dephlogisticated air. . . . In like manner, according to this hypothesis, the rationale of the production of dephlogisticated air from red precipitate is, that during the solution of the quicksilver in the acid and the subsequent calcination, the acid is decompounded, and quits part of its dephlogisticated air to the quicksilver, whereby it comes over in the form of nitrous air, and leaves the quicksilver behind united to dephlogisticated air, which, by a further increase of heat, is driven off, while the quicksilver re-assumes its metallic form." Yet he preferred to adhere to "the commonly received principle of phlogiston," because "it explains all phenomena at least as well as Mr. Lavoisier's." He says: "As adding dephlogisticated air to a body comes to the same thing as depriving it of its phlogiston and adding water to it, and as there are, perhaps no bodies entirely destitute of water, and as I know no way by which phlogiston can be transferred from one body to another, without leaving it uncertain whether water is not at the same time transferred, it will be very difficult to determine by experiment which of these opinions is the truest."

If we translate (as is often done) "deprived of phlogiston" by the word "oxidized," and "united to phlogiston" by "deoxidized," then we have Cavendish's view of the formation of water by exploding a mixture of dephlogisticated and inflammable airs presented thus: oxidized water + deoxidized water = water. In this way of stating the change, the process is regarded as a transference of oxygen from one substance to another.

Some of the experiments detailed by Cavendish in his memoir published in 1784 showed that water was formed when a mixture of two gases, then called dephlogisticated air and inflammable air, was exploded, and that, when the gases were present in the mixture in about the proportion of two volumes of inflammable air to one volume of dephlogisticated air, probably the whole of both airs disappeared and water was produced in their stead. Nevertheless I do not think that Cavendish gave an approximately final answer to the question which he set himself to solve in the memoir of 1784. His object was "to find out the cause of the diminution which common air is well known to suffer by all the various ways in which it is phlogisticated, and to discover what becomes of the air thus lost or condensed." The cause of the diminution which common air suffers when it is exploded with inflammable air was considered by Cavendish to be the removal from the common air of "water deprived of phlogiston"; and what became of the thing removed was supposed by him to be, that it received phlogiston from "phlogisticated water," and so, by a proper distribution of phlogiston, both the dephlogisticated and the phlogisticated water became merely water.

Cavendish was trammelled by the theory of phlogiston. Until that "principle" had been banished from chemistry no clear conception could be formed of chemical changes as orderly reactions between distinct and definite substances. When phlogiston had been abandoned, the accuracy and conclusiveness of Cavendish's experimental work became apparent, and his results were seen to be of first-rate importance.[1]

[1] In the memoir published in 1785, Cavendish showed very conclusively that "nitrous acid" is formed when a mixture of common air and dephlogisticated

If the views expressed by Boyle on elements and chemical action are compared with the conceptions of phlogisteans a hundred years later, a going back is noticeable in that hundred years towards vague principles and qualities, although at the same time chemistry was enriched by many new facts of great importance.   To co-ordinate the facts of the science, to describe these facts accurately, to express them in a language which should make it easy to put together facts that were similar and to keep apart those which were unlike, and at the same time to overthrow the phlogistic theory; these were the tasks waiting to be accomplished at about the beginning of the last quarter of the eighteenth century.   It is not often that the power of destroying and the power of reconstructing are united in so extraordinary a degree as they were united in Lavoisier, the greatest of all chemists.

---

air is subjected to the action of electric sparks, and that this acid is formed by the chemical union of phlogisticated and dephlogisticated airs. Cavendish regarded this chemical union as equivalent to the removal of phlogiston from phlogisticated air, which was thus, he said, " reduced to nitrous acid."

CHAPTER II.

THE WORK OF LAVOISIER IN ESTABLISHING THE EXISTENCE OF CHEMICALLY DISTINCT SUBSTANCES, AND ACCURATELY DESCRIBING CHEMICAL CHANGES AS REACTIONS BETWEEN THESE SUBSTANCES.

NOTWITHSTANDING the excellence of the methods practised by Boyle, and the pregnant conclusions drawn by him from the facts which he established; the accurate work of Black on the chemical processes which happen when chalk is changed to lime and lime becomes chalk; the many kinds of air which Priestley discovered and examined; the great variety and importance of the chemical facts brought to light by Scheele; the accurate measurements made by Cavendish of the volumes of inflammable air and dephlogisticated air which combine to form water; notwithstanding the large body of work done by remembered and forgotten inquirers into material changes during more than two thousand years,—chemistry had not yet become a science. No descriptions had yet been given of processes wherein changes of composition accompany changes of properties, sufficiently full and accurate to enable the essential points of likeness between particular cases of such changes to be stated in terms applicable to every case, and sufficiently suggestive to indicate the lines on which investigation should proceed, in order that new likenesses might be discovered and descriptions made more exact. The conception of composition, as we now understand it, had not taken form. Careful and searching examinations of a few chemical occurrences were required, and precise statements of the results were necessary, before satisfactory hypotheses could be constructed in terms of which fuller descriptions might be given of the facts estab-

lished by experiment. What was needed was not explanation but description; it is so easy to explain, so difficult to describe.

Let us turn to the works of the Master. Antoine Laurent Lavoisier was born in 1743: on May 5, 1794, it was decreed, "La République n'a pas besoin de savants," and the guillotine did its work.

The *Mémoires de l'Académie des Sciences* for the year 1770 contain a paper by Lavoisier entitled *Sur la Nature de l'eau et sur les expériences par lesquelles on a prétendu prouver la possibilité de son changement en terre*. The experiments which the alchemists interpreted as proving the possibility of changing water into earth were examined critically by the chemist Lavoisier. In the first part of this memoir he discusses the most important experiments which had been made, and indicates the points which require more careful examination; in the second part he gives an account of his own experiments. Lavoisier collected rain-water directly in vessels of glass and enamelled porcelain, at a distance from habitations and trees; he determined very carefully the specific gravity of this water, and found it to be almost the same as that of water of the Seine after one distillation. By evaporating 11 pounds (*livres*) of this water, he obtained $4\frac{1}{4}$ grains of a very light, greyish earth, from which he extracted 1 grain of common salt, leaving $3\frac{1}{5}$ grains of earthy matter. Hence he concluded that this rain-water contained $\frac{3}{10}$ grain of a tasteless earth, and $\frac{1}{11}$ grain of common salt, per pound. He distilled this rainwater eight times, and determined the specific gravity of the distillate obtained, and the weight of the earthy matter that remained in the distilling vessel, each time. The specific gravity of the distilled water decreased very slightly by each distillation; but this minute decrease was not proportional to the weight of the earthy matter that remained after each process. At this stage of his investigations Lavoisier said:[1]

"I thought I might draw one of two conclusions from that experiment: either that the earth I had separated by distillation was of such a nature

that it could be kept in solution by the water without increasing the weight thereof, or, at any rate, without increasing it as much as other substances do; or that the earth in question was not present in the water when I determined the weight of the water, that it had been formed during the process of distillation, in a word, that it was a product of the operation. For the purpose of determining with certainty to which of those opinions I ought to assent, no method seemed to me more sure than to make an exact repetition of the same experiments in hermetically closed vessels, keeping an exact record of the weight of the vessel and of that of the water which should be employed in the experiment. If the matter of fire passed through the glass and combined with the water, then, after many distillations, there must necessarily be an increase in the total weights of the materials, that is to say, in the combined weights of the water, the earth, and the vessel. Physicists know as a fact that the matter of fire increases the weight of bodies wherewith it is combined. The same result ought not to happen, if the earth was formed at the expense of the water or of the vessel; but, there must necessarily be a decrease of weight of the one or of the other of the two substances, and that decrease must be exactly equal to the quantity of earth which separated.''

Lavoisier had made for him a *pelican* [1] of white glass, with a stopper of crystal; this he cleaned, dried, and weighed very carefully on a balance specially constructed for him, which indicated somewhat less than 1 grain with a load of 5 or 6 pounds. Into this pelican he put the rain-water which had been distilled eight times; he heated the vessel on a sand-tray, from time to time removing the stopper lest the expanding air should break the apparatus; when he judged the expansion of the air in the vessel to be completed, he placed the stopper securely in its place, and allowed the apparatus to cool. When the vessel and its contents were cold he weighed them; thus, he obtained the weight of the water in the pelican (it was somewhat more than 3 *livres* and 14 *onces*). He now fastened the stopper very securely in its place (using a cement made of clay, boiled linseed oil, and amber, and covering this with a moistened bladder tied with string), and kept the water at 60° to 70° Réaumur (say about 80° C.) for 101 days.

The experiment was begun on October 24th, 1768, and continued until February 1st, 1769. After the heating had continued for more than 25 days the water remained clear.

---

[1] *Pelican* was the name given by the alchemists to a distilling vessel with a head from which proceeded two necks that returned into the lower part of the vessel. When a liquid was heated in this vessel, the vapours condensed in the head, and the liquid thus formed flowed back into the body of the vessel.

Lavoisier remarks, "je commençais à désespérer du succès de mon expérience"; but on November 20th several little solid specks appeared in the water, and these gradually increased in size until about the middle of December, when a fine solid began to settle to the bottom of the vessel. On February 1st Lavoisier stopped the process;[1] he removed the wrappings and the cement from the stopper, and weighed the pelican and its contents. The weight was the same as before the heating had begun. Here are Lavoisier's weighings:

Weight observed in pan A of balance.				Weight observed in pan B of balance.				Weight; mean.			
Livres.	Onces.	Gros.	Grains.	Livres.	Onces.	Gros.	Grains.	Livres.	Onces.	Gros.	Grains
5	9	4	44·50	5	9	4	39·00	5	9	4	41·75
Mean weight of the same pelican and the water in it before the digestion..........................								5	9	4	41·50
Difference................................											0·25

Lavoisier very carefully removed the stopper from the pelican: air rushed in with a hissing sound; this result confirmed the conclusion drawn from his quantitative experiments that air had not penetrated into the vessel during the process. At this stage of the work Lavoisier remarks:

"From the fact that the weight of the materials had not increased, the conclusion was natural that neither the matter of fire, nor any other exterior body had penetrated the vessel and combined with the water to form the earth. It remained to determine whether that earth originated from the destruction of a portion of the water, or from the destruction of some of the glass vessel. The precautions I had taken made it easy to decide this question. It was only necessary to determine whether it was the vessel, or the water contained therein, which had lost weight."

Lavoisier carefully removed all the water and the solid matter (setting these aside in a glass flask), and dried and weighed the pelican; it had lost 17⅖ grains.

"This completely proved that the earth separated during the digestion was produced from the substance of the vessel; that a simple dissolution of the glass had happened. But, to complete my purpose, it was necessary to compare the weight of the earth which separated during the digestion of the

---

[1] "Voyant que la quantité de terre qui s'était rassemblée était considérable, craignant, d'ailleurs, qu'il n'arrivât du vaisseau quelque accident, et que je ne perdisse en un instant le fruit d'une opération que je continuais depuis plus de cent jours, je crus qu'il était temps de mettre fin à l'expérience."

water with the decrease of the weight of the pelican. These two quantities ought, of course, to be equal; if a considerable excess should be found in the weight of the earth, it would be necessary to conclude that the whole of the earth had not come from the glass."

Lavoisier, therefore, separated all the earthy matter, dried, and weighed it; the weight was $4\frac{9}{10}$ grains, which was considerably less than the loss of weight suffered by the pelican. He then determined the specific gravity of the water that remained; it was slightly, but distinctly greater than the specific gravity of ordinary distilled water (in the ratio of 1,000,037 to 1,000,000). He concluded that the water contained something dissolved in it; he distilled this water in a glass alembic made in one piece, and when most of the water was removed, he placed what remained in a small glass vessel, evaporated to dryness, and obtained $15\frac{1}{2}$ grains of the same white earth as before.

Now $15\frac{1}{2}+4\frac{9}{10}=20\frac{2}{5}$; that is to say, the total quantity of earth obtained weighed $20\frac{2}{5}$ grains. The loss of weight of the pelican was $17\frac{2}{5}$ grains; the difference between these weights is 3 grains. Lavoisier attributed this difference to the solvent action of the water on the flask wherein it had been kept and on the glass alembic wherein it had been distilled, after it had been separated from the $4\frac{9}{10}$ grains of earthy matter.

Lavoisier made a superficial examination of the earthy matter obtained from the water, but he did not come to any very definite conclusions concerning its composition.

The most important conclusions which Lavoisier drew from the results of this investigation were these.

"That the greatest part, or perhaps the whole of the earth which is separated from rain-water by evaporation is due to the dissolution of the vessels in which the water was contained and evaporated."

"That the water does not in any way change its nature, nor acquire any new properties by repeated distillations; and it is far from being made so attenuated, as Stahl supposed, that it is able to escape through the pores of the glass vessel."

"That the substance of the glass vessel can be dissolved by the water and that, as is the case with all salts, there is a point of saturation beyond which the solution cannot proceed."

"That the earth which MM. Boyle, Eller, and Margraff obtained from water was nothing else than some of the glass brought down by evaporation; so that the experiments on which these physicists relied, far from proving

the possibility of changing water into earth, rather pointed to the conclusion that water is unchangeable."

I have given a somewhat full account of Lavoisier's memoir on the alleged change of water to earth in order that the reader may have a just conception of Lavoisier's method.

The investigation is merely an accurate description of facts; the "principles" of the "vulgar chymists," the "elements" of the "Peripateticks," are ignored; in the beginning of the memoir Lavoisier says:

"Je ne parlerai point de ce qu'ont écrit sur les éléments les philosophes des premiers siècles; . . . je passe à ce qui intéresse plus particulièrement les physiciens; je veux parler des faits."

I do not think it is too much to say that this memoir destroyed a great part of the experimental basis of alchemy, and established the one method by which chemical changes could be satisfactorily investigated; the method wherein use is constantly made of the balance; the method adumbrated by Boyle, and used by Black fifteen years before the publication of Lavoisier's research. The way was now cleared for applying the method to the examination of the changes of composition that occur when substances burn in air.

Lavoisier worked on this question, and on questions connected with it, from about 1772 until his death in 1794. He began by once more establishing the fundamental fact that the weight of material obtained by burning a combustible substance is very often greater than the weight of the substance itself. In his first note,[1] he attributed the gain in weight, which he observed when sulphur and phosphorus were burnt in air, to the combination of air with the vapours of these substances. He said he was convinced that the *calces* of metals weigh more than the metals from which they are formed, because the metals combine with air; and he confirmed this conclusion by reducing litharge in closed vessels, using "l'appareil de Hales," [2] and obtaining, "at the moment of the passage of the *calx* into metal, a considerable quantity of air."

Rey and Mayow, in the seventeenth century,[3] had assigned

[1] See *Œuvres*, vol. ii. p. 103.
[2] Practically the same as Priestley's pneumatic trough.
[3] See pp. 25–27.

the same cause to the same phenomenon.   Mayow indeed had gone further; he recognized two constituents in air, and supposed that it was that one he called "fiery air" which supported combustion; he could not, however, discover what had become of the "fiery air" when the burning was finished.

The problems before Lavoisier were to determine the composition of the air, to find whether the whole or a portion of the air was absorbed by burning substances, and to recover from the products of burning that which the combustible substance had absorbed.

Priestley had not solved these problems: Scheele could not free himself from the phlogistic trammels; certainly in 1781 he thought of sulphur as being decomposed by heating in air. Cavendish had performed exceedingly accurate experiments in 1781–82, in attempting to find an answer to the question, "What becomes of the air lost or condensed during the calcination of metals and in other similar processes?"; but his answer was inconclusive.

I am not concerned with the fruitless controversy about the occasions when Lavoisier acknowledged his indebtedness to Priestley, Cavendish, Black, and other English men of science, and the terms wherein he made these acknowledgments. Lavoisier certainly owed much to others, but science owes far more to him.

At the beginning of his work Lavoisier recognized very clearly the importance of studying the composition of the air, and the properties of the air that is absorbed during calcination. He says:

"The importance of that subject seems to me calculated to bring about a revolution in physics and in chemistry." [1]

He also saw that a plan was needed, and that he must proceed step by step in an ordered fashion.

"The works of the different authors I have just cited have given me separate portions of a great chain; they have furnished some of the links, but, to obtain continuity, it is necessary to make a series of experiments." [2]

[1] Lavoisier's *Registre de Laboratoire* (February 20th, 1773), quoted by Grimaux on p. 104 of his work *Lavoisier*, Paris, 1888.
[2] Quoted by Grimaux, *l. c.*, p. 104.

The first thing to be done was to prove conclusively that metals absorb the air, or a portion of it, when they are burnt. In his *Opuscules physiques et chimiques* (published at the end of 1773, or the beginning of 1774),[1] Lavoisier argued that if a metallic calx consists of metal *plus* air, then air must be disengaged in the change of the calx back to metal. He heated a mixture of 6 *gros* minium and 6 *gros* charcoal, and obtained 560 *pouces cubiques* of an air which he proved, by many reactions, to be the same as the air disengaged by the action of acids on chalk, that is, fixed air. Inasmuch as the charcoal had disappeared, Lavoisier concluded that part of the air produced was furnished by the charcoal. He then burnt phosphorus in air standing over mercury; he found that there was a limit to the quantity of phosphorus which could be burnt, that when more phosphorus was introduced (without letting air into the vessel), this phosphorus refused to burn, that about one fifth of the original volume of air had disappeared, and that the weight of the air which had disappeared was nearly proportional to the difference between the weight of phosphorus burnt and the weight of the white solid produced.[2] He concluded that about one fifth of the air had combined with the phosphorus. He determined the specific gravity of the air that remained after burning phosphorus, and found it to be slightly less than that of ordinary air.

Lavoisier obtained similar results by burning lead and mercury in enclosed volumes of air.

"I thought I could conclude from these experiments, that a portion of the air itself, or of a material substance of some kind contained in the air, in an elastic state, combined with the metals during their calcination, and that the increase of the weight of the metallic calce was due to that cause."

Lavoisier remarked that as his results were in contradiction to those obtained by Boyle (who supposed the increase in weight during calcination to be due to the combination of the metal with the matter of fire, p. 12), he felt it necessary to repeat his experiments more rigorously. The results of this repetition are contained in the *Mémoire sur la calcination de*

---

[1] See *Œuvres*, vol. ii. p. 89.
[2] Lavoisier examined this white solid, and found it to be nothing but "l'acide phosphorique concret."

l'étain dans les vaisseaux fermés, et sur la cause de l'augmentation du poids qu'acquiert ce métal pendant cette opération.[1]

The argument is this, A metal is calcined in a closed vessel; if "matter of fire" passes through the vessel and combines with the metal, the weight of the whole apparatus will be greater at the end than at the beginning of the operation; but if the calx is produced by the combination of the metal with a portion of the air in the vessel, the total weight will be unchanged throughout the operation; moreover, if the vessel is opened when the calcination is finished, air will rush in, and the total weight will then be greater than at the beginning of the process.

Lavoisier calcined tin in glass vessels. The vessel was weighed and the tin was weighed; the vessel with the tin in it was heated for a short time to drive out some of the air, then sealed, allowed to cool, and weighed. After heating until the tin melted, and keeping at this temperature until some time after the formation of a blackish powder seemed to have stopped, the apparatus was allowed to cool, and was weighed. The vessel was then opened very carefully (air was heard rushing in), and the whole was weighed again. The tin that remained unchanged was separated from the calx; the tin, the calx, and the vessel itself were weighed separately.

Some of the weighings taken from an experiment which Lavoisier tells us was made on February 14, 1774, are given on the next page.[2]

As the weight of air in the flask, after sealing and before beginning the calcination, was $15\frac{1}{3}$ grains, and as the weight of "air" absorbed by the tin was 3·12 grains, it followed that about one fifth of the total weight of air had combined with the tin.

Another experiment, wherein 8 *onces* of tin were used, and the flask had a capacity of about 250 *pouces cubiques*, gave exactly similar results, except that only from one ninth to one eighth of the total weight of air was absorbed by the tin.

---

[1] *Œuvres*, vol. ii. p. 105. (Read in November, 1774; deposited with the Academy, May, 1777.)

[2] Most of the weighings are the means of several; each substance was weighed first on one pan, then on the other pan of the balance; the weighings were often repeated after an interval of a few days. The flask used in this experiment had a capacity of 43 *pouces cubiques*.

	Onces.	Gros.	Grains.
Weight of tin..	8	0	0·00
Weight of flask..	5	2	2·50
Total weight..	13	2	2·50
Weight of apparatus and contents after some air was removed by heating................................	13	1	68·87
Hence weight of air removed by heating.........	0	0	5·63
Weight of the apparatus and its contents after calcination.	13	1	68·60
Weight before calcination.....................	13	1	68·87
Difference...............................	0	0	0·27
Weight of apparatus after calcination and after allowing air to enter................................	13	2	5·63
Weight of apparatus full of air before beginning calcination..	13	2	2·50
Hence total increase in weight produced by calcination..	0	0	3·13

	Onces.	Gros.	Grains.
Weight of unchanged tin after calcination...................	7	6	37·37
Weight of calx formed by calcination.	0	1	37·75
Hence weight of tin and calx after calcination..........	8	0	3·12
Weight of tin before calcination......	8	0	0·00
Hence increase in weight of tin caused by calcination...	0	0	3·12
Weight of flask alone after calcination	5	2	2·50
Weight of unchanged tin after calcination.........................	7	6	37·37
Weight of calx formed by calcination.	0	1	37·75
Hence total weight (sum of three weighings) after calcination..................	13	2	5·62
Total weight (sum of two weighings) before calcination...................	13	2	2·50
Hence increase in weight of tin caused by calcination......	0	0	3·12

In this memoir Lavoisier says he had made experiments which led him to think that that portion of the air which combines with metals during calcination is slightly heavier than atmospheric air, and that portion which remains after calcination is slightly lighter than atmospheric air. He acknowledges that his experiments ought to be repeated in flasks of different capacities, and that he ought to determine the exact relation between the quantity of air absorbed by a metal during calcination and the total quantity of air wherein the metal is calcined; "but experiments of this kind demand so much time and attention to make them satisfactory, they are so exhausting and require apparatus so troublesome to construct, that I have not as yet had the courage to pursue the work further." He adds that his experiments on calcining tin had suggested a new line of research; these experiments made him suspect that the air is composed of different substances, a suspicion confirmed by the work he had undertaken on the calcination of mercury and the revivification of the calx of that metal, and he thought he was in a position to assert that the portion of the air which combines with metals during calcination is that portion which can be breathed, whereas the portion which remains after calcination is "a kind of mephitic air incapable of maintaining the respiration of animals or the burning of substances." [1]

We now come to Lavoisier's *Mémoire sur la nature du principe qui se combine avec les métaux pendant leur calcination et qui en augmente le poids.* [2] The memoir opens thus:

"Do different kinds of air exist? Is it enough that a body should be in a state of permanent expansibility for it to count as a particular kind of air? Finally, the different airs found in nature, or formed by us, are these particular substances, or modifications of atmospheric air? Such are the main questions proposed in the plan I have formed for myself."

---

[1] It is interesting to compare the views of Lavoisier at this time (the end of 1774) with Priestley's phlogistic speculations (in 1775) about the " goodness " of the air he had obtained from red precipitate. (Compare, pp. 33–31.)

[2] Read to the Academy at Easter, 1775; re-read August, 1778. In a note Lavoisier says his first experiments on heating red precipitate were made in November, 1774, and these experiments were repeated in February and March, 1775. We know that Priestley visited Lavoisier in October, 1774, and told him of the new air he had obtained by heating red precipitate.

For an account of Bayen's experiments on heating calx of mercury, made in 1774, see Miss Freund's *A Study of Chemical Composition* [1904], pp. 41–43.

Lavoisier then says that he proposes to show that

"The principle which unites with metals during calcination, which increases the weights of them, which brings them into the state of calces, is nothing else than the most salubrious and the purest portion of the air; so that, if the air which has been entangled in combination with a metal again becomes free, it comes forth in a very respirable condition, and more fitted than atmospheric air for maintaining the inflammation and the combustion of bodies."

Most metallic calces, Lavoisier says, are reduced (that is, caused to become metals) only by heating with carbonaceous matter, or with some substance which contains what is called *phlogiston*. When the proper quantities of charcoal and calx are used, the whole of the charcoal disappears; hence the "fixed air" which is disengaged in these reductions is produced by the union of the air from the metallic calx and that from the charcoal; and we cannot justly conclude that the air which is in the calx before the action of the charcoal on it is the same as the air (fixed air) given off during the reduction.

These reflections led Lavoisier to turn his attention to those metallic calces which could be reduced without the addition of other substances. He tried calx of iron, but he found many difficulties. Then he chose calx of mercury; he remarks that everybody was aware that this substance could be reduced by heat alone.[1] By heating this substance with charcoal and obtaining fixed air, he proved *mercurius calcinatus per se* to be a true metallic calx.

One *once* of calx of mercury was then heated in a small flask having a capacity of two *pouces cubiques*. He obtained 7 *gros* and 18 *grains* of running mercury, and 78 *pouces cubiques* of a gas. Supposing, he says, that the total loss of weight (54 *grains*) was due to the production of the gas he collected, then each *pouce cubique* of that gas weighed a little less than $\frac{2}{3}$ *grain*, and the gas had nearly the same specific gravity as ordinary air. Lavoisier then examined the gas he had pre-

---

[1] It is, of course, to be remembered that Priestley had told Lavoisier of his experiments on heating calx of mercury. In Lavoisier's laboratory journal for February, 1776, to March, 1778, the gas obtained by heating calx of mercury is referred to as "l'air dephlogistique de M. Priestley."

pared from calx of mercury. The gas would not combine with water when agitated therewith; it did not produce a precipitate in lime-water; it did not combine with the fixed or volatile alkalis, nor did it decrease the caustic qualities of these alkalis. It could be used in the calcination of metals; it had none of the properties of fixed air; and combustible substances burnt in it brilliantly and rapidly.

Lavoisier concluded that this gas was purer than ordinary air, and that the principle which combined with metals during calcination was nothing else than the purest portion of the air we breathe. He also argued that fixed air was obtained in all reductions of metallic calces by charcoal, because the charcoal combined with the pure air in the calces; and he thought that all metallic calces would yield the same pure air as calx of mercury if they could be reduced without the addition of any foreign substance.

Finally, Lavoisier recalls the fact that the detonation of nitre with charcoal yields an air most of which is fixed air, and infers that nitre contains the same pure, respirable air as he had obtained from calx of mercury.

I would call the reader's attention at this point to the well-known experiment wherein Lavoisier heated 4 *onces* of mercury to boiling in 50 *pouces cubiques* of common air, as long as the formation of red scales was noticeable, and found that 7 to 8 *pouces cubiques* of the air disappeared, and 45 *grains* of a red powder were formed, which, when strongly heated, gave 41½ *grains* of mercury and 7 to 8 *pouces cubiques* of pure air that supported combustion and respiration. This experiment is described in Lavoisier's *Traité élémentaire de Chimie* (published in 1789). See *Œuvres*, vol. i. p. 36.

In his next memoir,[1] Lavoisier recalls his earlier experiments on burning phosphorus in an enclosed volume of air, wherein he showed that about one fifth of the air was absorbed by the phosphorus, and *l'acide phosphorique* was produced. Experiments suggested by these results, and by those recorded in the memoir "On the Nature of the Principle which combines

---

[1] *Mémoire sur l'existence de l'air dans l'acide nitreux*, April 20, 1776; deposited December, 1777.

with Metals during their Calcination," had now (he says) enabled him to assert

"That not merely air, but rather that portion of air which is the purest, enters into the composition of all the acids without exception; that it is that substance which produces their acidity, so that one may at pleasure remove or bestow the quality of acidity, according as one takes away or gives back the portion of air which is essential to their composition."

Lavoisier proposed to deal with the decomposition and the formation of different acids in a series of memoirs, beginning with nitric acid. The gases or airs produced by the reactions between metals and acids had been regarded as derived from the metals; Lavoisier said that these different kinds of air were produced by the decomposition of the acids themselves. He proposed to discover the composition of nitric acid by causing it to react with mercury, and studying the phenomena that presented themselves from the beginning of the reaction until the mercury, passing through the stages of a mercurial salt and red precipitate, should be reproduced as the metal. He caused weighed quantities of mercury and nitric acid (specific gravity 1·316) to react; collected and measured the air produced until the mercury was converted into a white salt, also the air given off during the change of this salt to *un beau précipité rouge*, and also the air formed while this red precipitate became metallic mercury. The weight of mercury obtained at the end of the experiment was the same, less a few grains, as the weight of mercury taken at the beginning; and certain volumes of the "nitrous air" described by Priestley, and the "pure air" obtained both by Priestley and Lavoisier himself from red precipitate, were produced.[1] Lavoisier then mixed measured volumes of nitrous air and pure air[2] over water; he noticed the instant production of red vapours, which at once dissolved in the water; and he proved the presence of nitric acid by adding alkali to the water, evaporating, and obtaining

---

[1] It is interesting to observe that Priestley attempted to repeat this experiment, and declared that there was a considerable loss of mercury in the process. (See preface to vol. iii. of *Observations and Experiments on Different Kinds of Airs.*)

[2] The volumes of these gases were not in the same proportion as the volumes he obtained by decomposing nitric acid. He gives reasons for this, but refers to future memoirs for details concerning the reactions between nitrous air and pure air.

crystals of nitre.   He also formed nitric acid by the reaction between nitrous air and ordinary air; but he found it necessary to use a volume of common air about four times greater than the volume of pure air he had employed to saturate the nitrous air; and he noticed that only about one fourth or one fifth of the common air disappeared, and that the residue would not maintain the combustion of burning substances or the respiration of animals.

Lavoisier regarded the experiments described in this memoir as proving that "nitric acid is nothing but nitrous air combined with a volume, almost equal to its own, of the purest portion of air, and with a considerable quantity of water: nitrous air, on the contrary, is nitric acid deprived of air and water."

Lavoisier speaks of the possibility of phlogiston playing some part in these changes.   Without daring to decide a question so important, he remarks that, as the mercury was precisely the same at the end of the operations as it was at the beginning, both in qualities and quantity, there was no sign of its having lost or gained phlogiston.

Referring to Priestley's conclusion, from his own experiments, that ordinary air "consists of the nitrous acid and earth" (see page 33), Lavoisier remarks that his experiments show "que ce n'est point l'air qui est composé d'acide nitreux . . . mais, au contraire, l'acide nitreux qui est composé d'air."

In a paper read to the Academy, April, 1777, Lavoisier returned to the subject of the combustion of phosphorus in ordinary air, confirmed the fact that about one fifth of the air was absorbed by the phosphorus, and proposed to call the air that remained *mofette atmosphérique*.   By adding to this *mofette atmosphérique* a volume of pure air equal to that absorbed by the burning phosphorus, he obtained ordinary air.   He also examined the acids produced by the burning of phosphorus and of sulphur, and showed that each contained more than half its weight of pure air.   In the same year he examined the reaction between mercury and sulphuric acid by a method similar to that he had used in studying the action of nitric acid on mercury; and he obtained, and to some extent examined, *l'acide sulfureux aériforme*.

Lavoisier's *Mémoire sur la combustion en général* (1777) contains some most excellent remarks on the use and abuse of systems in physical science.

"Systems, in physics . . . are but the proper instruments for helping the feebleness of our senses. Properly speaking, they are the methods of approximation which put us on the track of solving problems; they are the hypotheses which, successively modified, corrected, and changed according as they are contradicted by experience, ought some day to conduct us, by the method of exclusions and eliminations, to the knowledge of the true laws of nature."

He then proceeds to enunciate

"An hypothesis by the help whereof one explains, in a very satisfactory way, all the phenomena of combustion, of calcination, and even, in part, the phenomena which accompany the respiration of animals."

He says that four constant phenomena are observed during combustion: matter of fire or of light is disengaged [1] combustion occurs only when the combustible substance is in contact with certain kinds of air, especially that kind called *dephlogisticated air* by Priestley and *pure air* by Lavoisier; the burnt substance weighs more than the unburnt substance, and the increase in weight is proportional to the quantity of pure air that combines with the burning substance; the product of burning is either an acid or a metallic calx. In a memoir, presented to the Academy in 1777, entitled *Considérations générales sur la nature des acides*, Lavoisier says he can now assert that pure air enters into the composition of all acids; that there is no acid, *except perhaps that of common salt*,[2] which cannot be decomposed and reproduced, deprived of the principle of acidity or have that principle restored to it. By the expression *principle of acidity*, Lavoisier means oxygen. It is in this memoir that he proposes for the gas he had hitherto called pure air, the names *le principe acidifiant* and *le principe oxygine*. Oxygen, he says, combines with charcoal, and the product is the acid of chalk; the product of the combination of oxygen and sulphur is vitriolic acid; by combining with nitrous air, oxygen pro-

---

[1] By *the matter of fire*, Lavoisier at this time meant a subtile, imponderable fluid, supposed to be disseminated through everything, and capable of being released from its combination with one substance and either set free as heat, or combined with some other substance.

[2] Italics not in original.

duces the acid of nitre; phosphoric acid is formed by the union of oxygen with phosphorus, and the metallic calces, as a class, are produced by the combination of oxygen with the metals. Lavoisier then sketches the vast domain whereto these facts introduce the chemist, and indicates the kind of investigation needed in order to gain accurate knowledge of the combinations of oxygen, and the properties of the substances produced by these combinations.

In summing up the results of his experiments on the combinations of oxygen, towards the end of this memoir, Lavoisier regards oxygen as the substance which gives to all acids the property of acidity, and the other component (or components) of an acid as that which gives its particular properties to that acid; and he draws attention to the fact that although the product of the union of oxygen with a metal is generally a metallic calx, there are compounds of metals (iron and arsenic, for example), with a superabundance of oxygen, which have the properties characteristic of acids.

These statements show that although Lavoisier (in 1777) regarded oxygen as the acidifying principle, he clearly recognized that not all compounds of oxygen are acids, and he definitely connected the chemical properties of substances not only with the properties, but also with the relative quantities of their components. The definite way wherein he connected properties with composition is well illustrated in his memoir on the combination of oxygen with iron (1783). (See *Œuvres*, vol. ii. p. 565.)

I would ask the student to pay particular heed to the use Lavoisier makes of the expression *principle*, about the year 1780. He does not employ this term in the vague manner of the alchemists, but he uses it to mean exactly what we now convey by the words *element* and *compound*.

In his criticism of the phlogistic theory,[1] Lavoisier gives a clear account of the state of his experiments, and his views on combustion and phenomena related thereto in the year 1777. Stahl had proved that the property of being combustible can be transferred from one body to another: for instance, charcoal is

---

[1] *Réflexions sur le phlogistique* (published in 1783; see *Œuvres*, vol. ii. p. 623).

combustible and oil of vitriol is not; when charcoal is heated with oil of vitriol the combustible substance sulphur is produced, and the charcoal vanishes. Stahl supposed he had explained these facts by saying that the principle of combustibility passed from the charcoal to the oil of vitriol. This explanation was merely a very superficial and inadequate description of the change that occurred. Lavoisier gave a description of changes like this which was fuller, more exact, and more penetrative than Stahl's description. Lavoisier's experimental results convinced him that in order to acquire a knowledge of what happened in processes of combustion, and in processes like these, it was necessary to examine the changes of composition which accompanied the changes of properties, and that this examination must include measurements of the quantities of all the materials that took part in the changes.

Advancing from the quantitative examination of one chemical change to that of others like it, Lavoisier was able, about the year 1777, to describe many chemical processes fairly accurately and exhaustively. Of course he expressed the reactions which he examined in a language in keeping with the knowledge and the needs of his time; but, in 1777, he had given us the essentials of the language we use to-day, by establishing (although not yet clearly expressing) the conceptions of the *element* and the *compound*.

By abolishing the vague, constantly changing conception of phlogiston, Lavoisier made a great advance towards clearer and more suggestive descriptions of chemical changes than those of any other worker of his time. The clearer descriptions he gave of chemical occurrences led the way to new researches and new hypotheses, and these made possible yet clearer and more complete descriptions.

Among the most important of Lavoisier's memoirs, bearing directly on the conception of chemical changes as definite interactions of homogeneous substances, published between the years 1777 and 1785, are his two memoirs on the *decomposition and recomposition of water*,[1] and those on the *acid of carbon*,[2]

[1] Read to the Academy 1783 and 1784; see *Œuvres*, vol. ii. pp. 334, 360.
[2] *Œuvres*, ii. p. 403.

the *dissolution of metals in acids*,[1] the *precipitation of metals by one another*,[2] the *affinities of oxygen*,[3] and the *union of oxygen with iron*.[4] In these memoirs Lavoisier made accurate determinations of the compositions of several compounds, and of the quantities of definite substances which took part in various chemical reactions; he accounted for everything which entered into the reactions he studied, and he connected quantitatively the compositions of the systems before and after the changes. Lavoisier formed a vivid mental picture of chemical change by making minute studies of several definite interactions and connecting these with one another.

I ask the student's especial attention to the formulæ whereby Lavoisier expressed the compositions of systems of substances which react chemically. Lavoisier's formulæ show how completely he had put aside alchemical conceptions, and how full and clear was his presentation of chemical changes, in the early eighties of the eighteenth century. The system is explained and illustrated in his memoir on the dissolution of metals in acids.[5]

Take the reaction between iron and nitric acid dissolved in water. Lavoisier regarded nitric acid to be a compound of "nitrous air," oxygen and water; for iron he used the symbol $\male$. Let b express the ratio between the quantities of iron and nitric acid which react; then ab is the quantity of acid needed to dissolve a parts of iron. Now the quantity ab of nitric acid is composed of a certain quantity of water expressed by Lavoisier as $\dfrac{ab}{q}$, a certain quantity of oxygen which he expressed as $\dfrac{ab}{s}$, and a certain quantity of "nitrous air" expressed as $\dfrac{ab}{t}$. In order to moderate the reaction, Lavoisier dissolved the nitric acid in two parts of water. The symbols he used for water, oxygen, nitric acid, and nitrous air

---

[1] *Œuvres*, ii. p. 509.
[2] *Ibid.*, ii. p. 528.
[3] *Ibid.*, ii. p. 546.
[4] *Ibid.*, ii. pp. 557, 575.
[5] *Considérations générales sur la dissolution des métaux dans les acides.* (*Mém. de l'Acad.*, 1782, p. 492; *Œuvres*, ii. p. 509.)

were, ∇, $\oplus$, $\ominus$, and $\triangle$ respectively. The composition of the mixture before the reaction was expressed by Lavoisier thus:

$$\left(a\ \sigma\right)+\left(2ab\nabla+\frac{ab}{q}\nabla\right)+\left(\frac{ab}{s}\oplus+\frac{ab}{t}\triangle\right).$$

The many quantitative examinations he had made of the reactions between metals and nitric acid led Lavoisier to regard most of these reactions as consisting in the withdrawal of oxygen from the acid by the metal. He proposed to represent the quantity of oxygen withdrawn by the iron as $\frac{a}{p}\oplus$; this quantity he added to the a parts of iron, and removed from the $\frac{ab}{s}$ parts of oxygen, in the formula given above. The withdrawal of oxygen from the nitric acid was accompanied by the production of nitrous air; and as Lavoisier's experiments (at this time) led him to regard the quantity of nitrous air which was formed as almost equal to the quantity of oxygen which combined with the iron, he represented the nitrous air produced as $\frac{a}{p}\triangle$; this quantity was, of course, taken away from the $\frac{ab}{t}$ parts of nitrous air in the formula already given, because this quantity of nitrous air escaped.

To simplify matters, Lavoisier took the quantity of nitric acid used in his experiments as always one pound: hence, ab became equal to unity, and the formula which expressed the state of affairs in the solution after the reaction was the following:

$$\left(a\ \sigma+\frac{a}{p}\oplus\right)+\left(2\nabla+\frac{1}{q}\nabla\right)+\left(\frac{1}{s}\oplus-\frac{a}{p}\oplus+\frac{1}{t}\triangle-\frac{a}{p}\triangle\right).$$

"The parentheses," Lavoisier says, "express the manner of the grouping of the different kinds of molecules in the solution." Lavoisier's experiments had convinced him that one pound of nitric acid, diluted with two parts of water, dissolved ·2 pound of iron, at the ordinary temperature, or when very gently warmed; hence, as $ab=1$, $a=0\cdot2$ in the above formula. He found the value of p by dissolving weighed quantities of iron

in nitric acid, evaporating to dryness, heating the residue strongly, and weighing; the gain in weight was the weight of oxygen taken by the iron from the nitric acid.

Taking the mean value thus determined, Lavoisier deduced for the expression $\frac{a}{p}$ the value ·058. Another set of experiments gave him these results: $\frac{1}{q}=\frac{1}{2}$, $\frac{1}{s}=\frac{1}{4}$, $\frac{1}{t}=\frac{1}{4}$. Hence, $q=2$, $s=4$, and $t=4$. Substituting these values in his formula, and reducing the formula to its simplest expression (supposing always that one pound of nitric acid is used, and that the figures represent pounds and parts of pounds), Lavoisier wrote the formula thus:[1]

$$(·2\varfemale + ·058 \oplus) + (2·5\nabla) + (·192 \oplus + ·192 \triangle).$$

He tested this formula by calculating the quantity of iron which should be dissolved by a determinate quantity of nitric acid, and then determining the quantity actually dissolved by that amount of nitric acid. He obtained results which convinced him of the accuracy of his formula; but he noted certain refinements which should be introduced into the formula, provided the experimental methods were themselves more refined. "But then one would have a formula which would be too complicated, and that would be to introduce into chemistry too refined a geometry, a geometry which is as yet beyond its capacity."

Towards the end of this memoir Lavoisier mentions the investigations which he thinks the most important for gaining a clearer knowledge of the reactions that occur when metals dissolve in nitric, sulphuric, hydrochloric, and certain other acids. It is necessary to know with great accuracy, he says, the quantitative composition of water, the quantities of water, oxygen, and nitrous air which compose nitric acid, the quantities of water, sulphur, and oxygen whereof sulphuric acid is composed, and so on.

---

[1] The carefulness and exactness of Lavoisier's descriptions are well shown in his statement of what this formula expresses; it expresses the state of affairs that result when one pound of nitric acid, specific gravity, 1·29895, diluted with two parts of water, has reacted with enough iron to saturate the acid, at a temperature of about 10°.

Lavoisier's *Traité Élémentaire de chimie* was published in 1789. This work is a systematic treatise on chemistry. The facts of the science are arranged in an orderly manner; that accurate and far-reaching description of the one common feature of all material transformations, which is now called "the law of the conservation of mass," is the foundation of the system; chemical changes are not only said to be interactions of elements and compounds, they are described and analyzed as such interactions; the simple substances are enumerated and their compounds are classified; the relations of class to class are developed, and a consistent and suggestive nomenclature is used.

At last, after more than two thousand years of work and thought, a clear conception of the object of chemistry is gained; certain substances are recognized to be definite, distinct, and homogeneous; the supreme arbitrament of the balance is acknowledged; the study of the changes of properties and of composition has become a science. Lavoisier did not create nor did he revolutionize chemistry: he transformed it.

The object of chemistry is stated thus by Lavoisier: "In submitting to experiments the different substances found in nature, chemistry seeks to decompose them, and to bring them into a condition such that *their components can be examined separately*. . . . Chemistry advances towards its goal, and towards its perfection, by dividing, subdividing, and again subdividing, and we do not know what will be the limit of its victories. We cannot be certain that what we think to-day to be simple is indeed simple; all we can say is, that such or such a substance is the actual term whereat chemical analysis has arrived, and that with our present knowledge we are unable to subdivide further."[1]

Lavoisier gives a table (*Œuvres*, i. p. 135) of the simple substances. This table contains the names of thirty three substances. Omitting light and heat, and the three radicals, "radical muriatique, radical fluorique, radical boracique," there remain twenty eight substances: five of these (lime, magnesia, baryta, alumina, and silica) are now known to be compounds;[2] the remaining twenty three are to-day regarded as elements.[3]

---

[1] *Œuvres*, i. pp. 136, 137.

[2] It is interesting and instructive to notice that Lavoisier suggests that the earths would probably soon be found not to be simple substances; he thinks they may turn out to be metallic oxides, "oxygénés jusqu'à un certain point." Of the fixed alkalis, such as potash and soda, he remarks: "Ces substances sont évidemment composées, quoiqu'on ignore cependant encore la nature des principes qui entrent dans leur combinaison." (*L. c.*, p. 137.)

[3] These twenty three elements are: oxygen, nitrogen, hydrogen, sulphur, phosphorus, carbon, antimony, arsenic, bismuth, cobalt, copper, gold, iron,

The principle of the conservation of mass is assumed by Lavoisier in all his investigations. In considering the fermentation of fruit-juices, wherein carbonic acid gas and alcohol are produced, he says:[1]

"One sees that . . . it would first be necessary to become thoroughly acquainted with the analysis and the nature of the substances which can be fermented, and of those which are the products of fermentation. For nothing is created, either in the operations of art or in those of nature; and one may lay down the principle that in every operation there is an equal quantity of matter before and after the process, that the quality and the quantity of the principles are the same, and that there is nothing but certain changes, certain modifications. The whole art of experimenting in chemistry is founded on this principle; in all experiments one is obliged to suppose a true equality, or equation, between the principles of the substances which one examines and those which one obtains by analysis. Thus, since grape-juice gives carbonic acid gas and alcohol, I can say that grape-juice = carbonic acid + alcohol."

This passage, and the way it is introduced in the midst of an experimental examination of a chemical process, are very characteristic of Lavoisier. He does not begin by laying down certain propositions deduced from what are called "first principles"; he simply accurately describes chemical changes, and from time to time he makes generalized statements, which are at once comprehensive descriptions of the facts he is examining, and (in some cases) of so many other similar facts that they are found to be true laws of nature.

These seem to me the chief marks of the work of Lavoisier: an extraordinary thoroughness in each investigation; a lucidity of description of facts independently of hypotheses, until hypotheses become necessary; a close connexion between all investigations bearing on the same subject; a power of seizing every problem from the inside and ignoring its unessential parts; a vivid imagination; and an ever-present realization that all facts are not of equal value.

The question, What is a chemically homogeneous substance? was not distinctly enunciated until it had been partly answered; and an answer began to be given to this question only when the other question was considered, What happens when chemically homogeneous substances interact? The older workers were chiefly concerned with the reactions of substances; they asked,

---

lead, manganese, mercury, molybdenum, nickel, platinum, silver, tin, tungsten, and zinc. The student should notice that Lavoisier (*Œuvres*, i. p. 138) gives a list of radicals of various acids " which enter into combination after the manner of simple substances "; most of these are radicals of organic acids: he says these radicals are composed of carbon and hydrogen, that many of them also contain nitrogen, and some of them also contain phosphorus.

[1] *Œuvres*, i. 101.

How can we explain those changes of properties which we observe? The investigators of the eighteenth century began to see that the only way of answering this question was by examining the compositions of the substances whose properties changed. It was one of the signal merits of Lavoisier that he not only saw the close interdependence of the study of changes of composition and the examination of changes of properties, but he also gave definite and practical meaning to the expressions *chemical composition* and *chemical reaction*.

To-day it is possible to recognize a certain likeness between the saying of Stephanus of Alexandria (about 620), "it is necessary to deprive matter of its properties in order to draw out its soul," and the statement of Lavoisier (1789) that the object of chemistry is "to decompose the different natural bodies, and . . . to examine separately the different substances which enter into their combination." The first statement rested on a sweeping and superficial glance over an intricate maze of occurrences, and it produced little accurate knowledge. The second statement was a result of the penetrating study of a few detached events; it was a translation of the first statement into expressions which could be directly applied to a vast number of particular phenomena, and in a few years it produced a science.

Alchemy was a phase in the search for invariants; it was a stage in the endeavour to find *a* property of bodies, measurable and remaining constant while other properties changed, and such that its relations to other properties could be quantitatively expressed. The search advanced slowly; it wandered into many side-paths and tried many blind-alleys; at last, by the genius of such men as Boyle, Stahl, Black, Priestley, and Cavendish, the quest became concentrated, and the announcement of the achievement of the invariant took definite form in the words of Lavoisier: "The quantity of matter is the same at the end as at the beginning of every operation; the quality and the quantity of the principles are unchanged."

The alchemical distinction of qualities and substance changed to the chemical distinction of qualities and composition. Since the latter years of the eighteenth century, a thing, a substance,

is an assemblage of definite and measurable qualities; and the composition of a substance is the various assemblages of qualities into which that substance can be separated and by the union of which it can be produced. The criterion of separation is found in measurements of that quality which we call mass. That we may have a convenient language wherein to express facts of composition, we are accustomed to speak of mass as measuring quantities of matter, and assemblages of properties as varieties of matter; and so, to some extent, we have reverted to the alchemical notion of substance as a reality apart from what is perceived by the senses.

CHAPTER III.

THE MARKS OF THE TWO CLASSES OF CHEMICALLY DISTINCT SUBSTANCES, ELEMENTS AND COMPOUNDS; THE LAWS OF CHEMICAL COMBINATION; AND THE DALTONIAN ATOMIC THEORY.

LAVOISIER had clearly recognized certain substances as "the actual terms whereat chemical analysis had arrived," as not divisible by the methods then known. He had also recognized other substances, themselves physically homogeneous, as composed of definite quantities of these simple substances; he had formed a vivid and practically applicable presentation of chemical changes as combinations and separations of a limited number of simple substances; and he had realized for himself, and those who were to follow him, the principle of the conservation of mass.

It was necessary to examine the simple substances, and the products of their chemical union, more rigorously, and to express the compositions of these products in an intelligible, consistent, and suggestive language. Fuller answers to the questions—What is an element? What is a compound?—were to be given by measuring the quantities of elements that combine to form definite quantities of compounds. The next phase of the study of the transformations of matter was the quantitative examination of the compositions of compounds.

To follow the development of this part of our subject, we must glance at some of the earlier work which helped to prepare the way for the great leap forwards made by Dalton. And here, as everywhere in chemistry, we find that the study of reactions is closely interwoven with the study of composition.

The term *acid* seems to have been applied in the first instance to vinegar; it was then extended to various sour substances which resembled vinegar in their actions on other substances. Certain properties of the liquors obtained by lixiviating wood-ashes and the ashes of sea-plants were known to the ancients, and the name *alkali* was applied, sometime during the Middle Ages, to the substances obtained by evaporating these and similar liquids. In 1640 Van Helmont spoke of the saturation of an alkali by a definite quantity of an acid. In 1732 Boerhave recognized that the product of the saturation of potash-lye by an acid was a definite substance different from either of the things by whose union it was formed. In 1744 Rouelle extended the meaning of the term *salt*, which had been used very vaguely, and spoke of a salt as the product of the union of any acid with a *base*, a term used by Rouelle to include alkalis, earths, metallic substances, and oils. He distinguished degrees of saturation of an acid by a base, and recognized three clasess of salts, "sels neutres parfaits ou salés," "sels neutres avec excès ou surabondance d'acide," and "sels neutres qui ont une trés petite quantité d'acide." Rouelle distinctly said that a definite quantity of acid always combined with a definite quantity of base, to whatever class of salts the product of the reaction belonged.

During the years from 1791 to 1802, J. B. Richter published a treatise, in eleven parts, entitled *Ueber die neurn Gegenstände der chemie*. Richter's work will be described in the chapter on *Chemical Equivalency*: at present I give merely a very short account of some of it bearing on the subject of composition. Richter made a series of determinations of the weights of various bases neutralized by constant weights of several acids, and the weights of various acids neutralized by constant weights of several bases. The following statement, which is a free translation of Richter's words, summarizes his results.

Let P be the mass of one acid which neutralizes the masses a, b, c, d, e, of various bases; and let Q be the mass of another acid which neutralizes the masses α, β, γ, δ, ε, of the same bases; also let the neutral salts $P+a$ and $Q+\beta$, $P+a$ and $Q+\gamma$, $P+e$ and $Q+\alpha$, etc., decompose one another so that the products

are neutral; then the ratio of the masses a, b, c, d, e, is the same as the ratio of the masses α, β, γ, δ, ε.

Richter also determined that the weights of fifteen metals which dissolved in a constant weight of sulphuric acid, to form neutral salts capable of mutual reaction to produce other neutral salts, were in the same ratio as the weights of these metals which dissolved in the same constant weight either of hydrochloric acid or of nitric acid, to form neutral salts. Richter arranged his results on the formation of neutral salts, by the dissolution of metals in acids, in this form:

	1000 parts of Sulphuric Acid.	1000 parts of Hydrochloric Acid.	1000 parts of Nitric Acid.
dissolve	a parts of copper	e parts of copper	j parts of copper
and	b " " bismuth	f " " bismuth	k " " bismuth
neutral-	c " " antimony	g " " antimony	l " " antimony
ize	d " " tin	h " " tin	m " " tin

He said that the ratios $a:b:c:d$, $e:f:g:h$, and $j:k:l:m$ were the same.

That the composition of every chemical compound is constant seems to have been taken for granted by Lavoisier; and the investigations of chemists who came after him confirmed this supposition.

But, in 1803, Berthollet, in his *Essai de Statique Chimique* (a work of first-rate importance which will be considered in Chapter XIV of this book), asserted that only in some cases, and under special conditions, do elements and compounds combine in fixed proportions, and the general rule is that the quantities of chemically distinct substances which combine vary continuously between certain limits. In a series of publications from 1801 to 1809, Proust [1] (1755–1826) combatted Berthollet's statement, and succeeded in proving, by quantitative analyses, that the constituents of many oxides, sulphides, and salts are combined in fixed proportions. Proust distinguished true chemical compounds, whose constituents are combined in constant proportions, from

---

[1] *Journal de Physique*; some also in *Annales de Chimie*; and translations of several in *Nicholson's Journal* for 1802, 1806, 1807, and 1810. The principal compounds dealt with by Proust were of cobalt, copper, gold, nickel, silver, and tin.

solutions and mixtures the components whereof may be present in different proportions; he showed, by accurate analyses, that many substances supposed to be compounds were really mixtures.

When Dalton [1] began his work on the compositions of compounds, the controversy between Berthollet and Proust was not finished; but by the time of the publication of his book, *A New System of Chemical Philosophy* (1808), many chemists were almost satisfied that every compound has a constant composition, and that combination proceeds between elements, or compounds, in determinate stages.

In the preface [2] to the first part of his *New System* [3] Dalton says: "In 1803 [the author] was gradually led to those primary laws which seem to obtain in regard to heat, and to chemical combinations, and which it is the object of the present work to exhibit and elucidate. A brief outline of them was first publicly given the ensuing winter in a course of Lectures on Natural Philosophy, at the Royal Institution in London." Among the MSS. found in the rooms of the Literary and Philosophical Society of Manchester, about 1896, was a number of books containing Dalton's laboratory and lecture notes. Copious extracts from these books have been published by Sir Henry Roscoe and Mr. Arthur Harden.[4] Dalton's notes for the lecture delivered by him at the Royal Institution on January 27th, 1810, on the subject of the *Chemical Elements*, are given in full in Roscoe and Harden's book. In these notes Dalton says:

"Having been long accustomed to make meteorological observations, and to speculate upon the nature and constitution of the atmosphere, it often struck me with wonder how a *compound* atmosphere, or a mixture of two or more elastic fluids, should constitute apparently a homogeneous mass, or one in all mechanical relations agreeing with a simple atmosphere. Newton had demonstrated clearly . . . that an elastic fluid is constituted of small particles or atoms of matter, which repel each other by a force increas-

[1] John Dalton, born 1766, died 1844.
[2] This preface is dated May, 1808.
[3] *A New System of Chemical Philosophy.* Part I. By John Dalton. (Manchester, 1808; Part II, 1810; Part III, 1827.)
[4] *A new view of the origin of Dalton's Atomic Theory; a Contribution to Chemical History.* By Henry E. Roscoe and Arthur Harden. (London, Macmillan & Co., 1896.)

ing in proportion as their distance diminishes. But modern discoveries having ascertained that the atmosphere contains three or more elastic fluids, of different specific gravities, it did not appear to me how this proposition of Newton would apply to a case of which he, of course, could have no idea."

At the time when Dalton was writing, the view prevailed that one kind of gas in the atmosphere dissolved another kind, by virtue of a weak chemical affinity, and that the indefinite compound so formed dissolved water. Attempting to present this view clearly to himself, "and to reconcile or rather adapt this chemical theory of the atmosphere to the Newtonian doctrine of repulsive atoms or particles," Dalton says, "I set to work to combine my atoms on paper." But he "soon found that the watery particles were exhausted"; he then combined the atoms of oxygen and nitrogen, one to one, but, he says, "I found in time my oxygen failed. I then threw all the remaining particles of azote into the mixture, and began to consider how the general equilibrium was to be obtained." But manipulate the atoms as he would, he could not obtain an atmosphere of the same relative density throughout. "In short," he says, "I was obliged to abandon the hypothesis of the chemical constitution of the atmosphere altogether, as irreconcilable to the phenomena." In 1801, Dalton "hit upon an hypothesis which completely obviated the difficulties" of the chemical view: "According to this, we were to suppose that the atoms of one kind did *not* repel the atoms of another kind, but only those of their own kind. This hypothesis most effectually provided for the diffusion of any one gas through another, whatever might be their specific gravities, and perfectly reconciled any mixture of gases to the Newtonian theorem."

But the new hypothesis, Dalton says, "had some improbable features."

"Upon reconsidering this subject, it occurred to me that I had never contemplated the effect of *difference of size* in the particles of elastic fluids. By *size* I mean the hard particle at the centre and the atmosphere of heat taken together. If, for instance, there be not exactly the same number of atoms of oxygen in a given volume of air, as of azote in the same volume, then the *sizes* of the particles of oxygen must be different from those of azote. And if the *sizes* be different, then on the supposition that the repulsive power is heat, no equilibrium can be established by particles of unequal sizes pressing

7

against each other. This idea occurred to me in 1805.[1] I soon found that the *sizes* of the particles of elastic fluids *must* be different. For a measure of azotic gas and one of oxygen, if chemically united, would make nearly *two* measures of nitrous gas, and those *two* could not have *more* atoms of nitrous gas than the *one* measure had of azote or oxygen. Hence the suggestion that all gases of different kinds have a difference in the *size* of their atoms; and thus we arrive at the reason for that diffusion of every gas through every other gas, without calling in any other repulsive power than the well-known one of *heat*." Dalton then proceeds: "The different *sizes* of the particles of elastic fluids under like circumstances of temperature and pressure being once established, it became an object to determine the relative *sizes* and *weights*, together with the relative *number* of atoms in a given volume. This led the way to the combinations of gases, and to the *number* of atoms entering into such combinations. . . . Thus a train of investigation was laid for determining the number and weight of all chemically elementary principles which enter into any sort of combination one with another."

When Dalton tells us that, in trying to reconcile "the hypothesis of the chemical constitution of the atmosphere" with the fact that the atmosphere is homogeneous throughout, he "set to work to combine [his] atoms on paper," and soon found that "the watery particles were exhausted," and "in time [his] oxygen failed," it is evident that he must have formed some hypothesis whereby he thought he could determine the relative numbers of the atoms of the constituents of the atmosphere.[2] What was that hypothesis? On page 188 of the *New System*, Dalton says:

"At the time I formed the theory of mixed gases, I had a confused idea, as many have, I suppose, at this time, that the particles of elastic fluids are all of the same size; that a given volume of oxygenous gas contains just as many particles as the same volume of hydrogenous; or if not, that we had no data from which the question could be solved."

It seems probable, then, that when Dalton began to think about the constitution of the atmosphere, he assumed the numbers of the atoms of the constituents of the atmosphere to be proportional to the volumes of these constituents in a determinate volume of air. As he was unable to apply this hypothesis successfully to the facts concerning the constitution of the atmos-

---

[1] Roscoe and Harden (*l. c.*, p. 25) say that " this date [1805] must be a clerical error for 1803, since he communicated an account of the atomic theory to Thomson in 1804, and [as his laboratory note-book shows] he had worked out a table of the diameters of the atoms in September, 1803."

[2] This is pointed out by Roscoe and Harden (*l. c.*, p. 18).

phere he abandoned it, and adopted the hypothesis that the sizes of the particles of elastic fluids are not the same, or, what was the same thing for Dalton, equal volumes of elastic fluids do not contain equal numbers of particles. He examined this hypothesis in the light of what he took to be facts concerning the combining volumes of certain gases, and he says:

"I became convinced that different gases have *not* their particles of the same size; and that the following may be adopted as a maxim, till some reason appears to the contrary: namely, *That every species of pure elastic fluid has its particles globular and all of a size; but that no two species agree in the size of their particles*, the pressure and temperature being the same." [1]

The instance of combining volumes given by Dalton is the formation of "nitrous gas," now called nitric oxide (*see* p. 78). Probably he had other cases of combinations of gases in his mind when he announced the "maxim" quoted above; for he says (*New System*, p. 188): "From a train of reasoning similar to that exhibited on page 71 [concerning the volume-composition of nitrous gas], I became convinced that different gases have *not* their particles of the same size. . . ."

In view of Dalton's treatment of Gay-Lussac's "law of combination by volume," to be considered in the next chapter, I think it is important to notice that the mental picture which Dalton formed of the atom, and the atomic constitution, of a gas forced him to conclude that if equal volumes of gases contain equal numbers of atoms, then the atoms of all gases must be the same size. But it was on the conviction that "no two species of elastic fluids agree in the size of their particles," he had laid "a train of investigation for determining the *number* and *weight* of all chemically elementary principles which enter into any sort of combination one with another."

What, then, was the conception of the atom formed by Dalton, and by what method did he measure the relative sizes and weights of atoms? In an entry in his laboratory notebook,[2] dated September 6th, 1803, Dalton says: "The ultimate atoms of bodies are those particles which in the gaseous state are surrounded by heat; or they are the centres or *nuclei* of the

---

[1] *New System*, p. 188.   [2] Roscoe and Harden, *l. c.*, p. 27.

several small elastic globular particles." This conception is amplified in the *New System* thus (p. 147):

"A vessel full of any pure elastic fluid presents to the imagination a picture like one full of small shot. The globules are all of the same size; but the particles of the fluid differ from those of the shot in that they are constituted of an exceedingly small central atom of solid matter, which is surrounded by an atmosphere of heat, of great density next the atom, but gradually growing rarer according to some power of the distance; whereas those of the shot are globules uniformly hard throughout, and surrounded with atmospheres of heat of no comparative magnitude." Again (p. 188): "By the size or volume of an ultimate particle, I mean . . . the space it occupies in the state of a pure elastic fluid; in this sense the bulk of the particle signifies the bulk of the supposed impenetrable nucleus, together with that of its surrounding repulsive atmosphere of heat."

And again (pp. 189, 190): "When we contemplate upon the disposition of the globular particles in a volume of pure elastic fluid, we perceive it must be analogous to that of a square pile of shot; the particles must be disposed into horizontal strata, each four particles forming a square: in a superior stratum, each particle rests upon four particles below, the points of its contact with all four being 45° above the horizontal plane, or that plane which passes through the centres of the four particles. On this account the pressure is steady and uniform throughout. But when a measure of one gas is presented to a measure of another in any vessel, we have then a surface of elastic globular particles of one size in contact with an equal surface of particles of another: in such case the points of contact of the heterogeneous particles must vary all the way from 40° to 90°; an intestine motion must arise from this inequality, and the particles of one kind be propelled amongst those of the other. The same cause which prevented the two elastic surfaces from maintaining an equilibrium, will always subsist, the particles of one kind being from their size unable to *apply properly to the other*, so that no equilibrium can ever take place amongst the heterogeneous particles. The intestine motion must therefore continue till the particles arrive at the opposite surface of the vessel against any point of which they can rest with stability, and the equilibrium at length is acquired when each gas is uniformly diffused through the other."

I think that, about the year 1808, Dalton had formed a mental picture of the atomic constitution of gases, and mixtures of gases, from considering some physical properties of gases, and the volumes of certain gases which combined with one another. Thinking of the atoms of gases as globular particles touching one another, Dalton found the diameter of an atom (relatively to the diameter of an atom of hydrogen) by dividing the weight of the atom (referred to hydrogen as unity) by the density of the gas (also referred to hydrogen as unity), and extracting the

cube root of the quotient.[1] The result, that the diameters of different kinds of atoms are not the same, confirmed Dalton's conviction that equal volumes of gases do not contain equal numbers of atoms.

Now comes the important question: How did Dalton determine the relative *weights* of atoms?

Roscoe and Harden (*l. c.*, p. 28) give an extract from his laboratory note-book, dated September 6th, 1803, wherein Dalton says:

> "From the composition of water and ammonia we may deduce ult. at. azot 1 to oxygen 1·42:
>> Ult. atom of nit. gas should therefore weigh 2·42 azot.
>> Ult. atom of oxygen   "   "   "   1·42 oxygen.[2]
>
> According to this 1 oxygen will want 1·7 nitrous.

	Sulph.		Oxy.	
Chenevix.	61½	+	38½	= sulphuric A.
Then.	61½	+	19¼	should be sulphureous.

> This gives ult. part. of sulphur to oxy. 3·2:1 nearly.

	Sulph.		Oxy.	
Thenart	56	+	44	
	56	+	22	sulphureous.
Fourcroy says.	85	+	15	= sulphureous."

On the next page of the note-book is given a table of the relative weights of the ultimate atoms of four elements and ten compounds. According to Roscoe and Harden,[3] the data from which Dalton concluded that an atom of oxygen is 1·42 times heavier than an atom of nitrogen were an analysis of ammonia made by Austin,[4] and an analysis of water made by Lavoisier. Austin's analysis gave the weight of the nitrogen as four times that of the hydrogen in ammonia; Lavoisier's analysis gave the ratio of the weights of hydrogen and oxygen in water as 1:5·66. Dalton assumed an atom of ammonia to be constituted of one atom of hydrogen and one atom of nitrogen. hence the atomic weight of nitrogen was 4, that of hydrogen being unity: he also assumed an atom of water to be constitued of single atoms of hydrogen and oxygen; hence the atomic weight of

---

[1] *New System*, p. 226, note.
[2] The word oxygen should evidently be *azot*.
[3] *l. c.*, pp. 84, 85. (References are given to Dalton's note-book.)
[4] Published in *Phil. Trans.* for 1788.

oxygen was 5·66, that of hydrogen being unity. Then, as 4 : 5·66 = 1 : 1·42, an atom of oxygen was 1·42 times heavier than an atom of nitrogen. In concluding that an atom of nitrous gas (nitric oxide) is 2·42 times heavier than an atom of nitrogen, Dalton again assumed the simplest possible atomic constitution for the compound under consideration. (One atom of nitrogen = 1, *plus* one atom of oxygen = 1·42, gives one atom of nitrous gas = 2·42.) Again, when he said "1 oxygen will want 1·7 nitrous," Dalton assumed that a single atom of nitrous gas (nitric oxide) combines with a single atom of oxygen (the ratio 2·42 : 1·42 = 1·7 : 1 nearly.) Chenevix's analysis of sulphuric acid (sulphur trioxide) gave the ratio of oxygen to sulphur as 1 : 1·6 nearly; in concluding that an atom of sulphur is nearly 3·2 times heavier than an atom of oxygen, Dalton assumed that the other compound of sulphur and oxygen, with less oxygen than sulphuric acid, must contain half as many atoms of oxygen as sulphuric acid, and that, as atoms are indivisible, an atom of sulphuric acid must contain two atoms of oxygen.

About six weeks after making the entry in his note-book quoted above, Dalton read a paper to the *Literary and Philosophical Society of Manchester*,[1] wherein he says: "An enquiry into the relative weights of the ultimate particles of bodies is a subject, as far as I know, entirely new; I have lately been prosecuting this enquiry with remarkable success. The principle cannot be entered upon in this paper; but I shall just subjoin the results, as far as they appear to be ascertained by my experiments." He then gives a "Table of the relative weights of the ultimate particles of gaseous and other bodies." This table contains the atomic weights of seven substances in addition to those given in the table of September 6th. In every case (except, of course, hydrogen) the values are different in the two tables. An examination of the atomic weights of various elements and compounds given by Dalton in this paper shows that he deduced these values by making certain assumptions regarding the numbers of elementary

---

[1] Read October 21st, 1803; published in 1805.

atoms which combine to form the atoms of compounds. The two principal assumptions implied in his results may be stated thus: (I) when only one compound of two elements is known, that compound has the simplest possible atomic constitution, it is composed of a single atom of each element; (II) when two gaseous compounds of a pair of elements are known, one of these (generally the compound which is specifically the the lighter) is composed of a single atom of each element, and the other is composed of two atoms of one of the elements and one atom of the other element. The second proposition, when extended to several compounds of two elements, is the law of multiple proportions stated in the language of atoms.[1]

To me it seems clear that what we now call *the law of multiple proportions* was included in Dalton's conceptions of the atom and the atomic constitution of compounds, and he did not arrive at this law from considering the analyses of compounds only. Indeed Dalton does not formulate the law of multiple proportions, nor any other of the generalized statements of facts we now know as *the laws of chemical combination*. These laws are included in his atomic theory as presented in the *New System;* they are special applications of the theory to certain aspects of chemical change.[2]

---

[1] It is worthy of notice that, although the table which appears in the paper read by Dalton on October 21st, 1803, contains the atomic weights of two compounds of carbon and hydrogen, we know, from Dalton's statement in *New System*, p. 445, and from the evidence of his note-book (see Roscoe and Harden, p. 29), that Dalton's experiments on these compounds were not made until the summer of 1804. Hence, the values for the atomic weights of the two compounds in question must have been added by Dalton before the paper was published in 1805; and also, to quote Roscoe and Harden (p. 29): "This disposes once and for all of the opinion commonly held, founded on Thomson's statement, that the atomic theory was suggested by a comparison of the analyses of marsh gas and olefiant gas. . . . " If it were possible to have any doubt that the theory was not suggested by the analyses of these gases, that doubt must be removed by Dalton's own words (*New System*, pp. 444–5): "No correct notion of the constitution of the gas about to be described [marsh gas], seems to have been formed till the atomic theory was introduced and applied in the investigation."

[2] An interesting example of Dalton's dealing with analytical data is furnished by his treatment of the compounds of nitrogen and oxygen (*New System*, pp. 316–319). After saying that it was usual to begin with the compound which contains least oxygen, he writes: " Our plan requires a different principle of arrangement; namely, to begin with that which is most simple, or which consists of the smallest number of elementary particles, which is commonly a binary compound, and then to proceed to the ternary and other higher compounds." The specific gravities of the compounds led him to conclude that " nitrous gas " (nitric oxide) is a binary compound. " Let us now see," he says, " how far

It is true that in a paper published in the *Memoirs of the Literary and Philosophical Society of Manchester* for 1805, and marked as having been read November 12th, 1802, Dalton gives an account of experiments on the combination of nitrous gas (nitric oxide) with the oxygen of the air, and says:

"These facts clearly point out the theory of the process: the elements of oxygen may combine with a certain portion of nitrous gas, or with twice that portion, but with no intermediate quantity. In the former case *nitric* acid is the result; in the latter *nitrous* acid: but as both these may be formed at the same time, one part of the oxygen going to *one* of nitrous gas, and another to *two*, the quantity of nitrous gas absorbed should be variable."

We have here a special case of the law of multiple proportions stated without reference to any theory of the atomic constitutions of the compounds concerned. Although the paper was read in November, 1802, it was not published until 1805. Dalton's note-book shows that in April, 1803, he was not certain about the volumes of nitrous gas and oxygen which combine; moreover, the note-book makes clear that in September, 1803, Dalton was trying experiments with nitrous gas and oxygen, and was comparing his results with those of Cavendish and of Lavoisier without coming to final conclusions regarding the compositions of the products; and, lastly, the numbers given in the paper published in 1805 (although read in 1802) are found in the entries in the note-book from October 10th to November 13th, 1803, that is about a month after

the facts already known will corroborate these observations." He tabulates the compositions of three of the compounds from the data of analyses by Davy and by Cavendish, and states the ratios of the weights of nitrogen and oxygen, " reduced to the determined weight of an atom of oxygen, 7."

RATIOS.

Nitrous gas (nitric oxide)	$\left\{ \begin{array}{l} 6{\cdot}1{:}7 \\ 5{\cdot}5{:}7 \\ 5{\cdot}1{:}7 \end{array} \right.$	
		} Davy.
Nitric oxide (nitrous oxide)	$\left\{ \begin{array}{l} 2\times6{\cdot}1{:}7 \\ 2\times5{\cdot}7{:}7 \\ 2\times5{\cdot}4{:}7 \end{array} \right.$	
Nit. acid (nitrogen dioxide)	$\left\{ \begin{array}{l} 5{\cdot}8{:}7\times2 \\ 5{\cdot}9{:}7\times2 \\ 5{\cdot}4{:}7\times2 \\ 4{\cdot}7{:}7\times2 \end{array} \right.$	} Cavendish.

" This table," says Dalton, " corroborates the theoretic views above stated most remarkably."

Dalton had arranged his first table of atomic weights. The conclusion which Roscoe and Harden (*l. c.*, p. 34) draw from these facts seems to me well justified: " The evidence which can be gathered . . . goes to show that both the experimental results and the explanation, as in the case of the carburetted hydrogen, are of a later date than that upon which the paper was read." [1]

When we come to the fuller statement of his atomic theory given by Dalton in the chapter " On Chemical Synthesis," in the *New System* (pp. 211–216), we find the assumptions implied in the entry in his note-book (quoted on p. 81), and in the paper read October 21st, 1803, laid down in the form of " general rules," which he says " may be adopted as guides in all our investigations respecting chemical synthesis."

The most important rules are these:

"1st. When only one combination of two bodies can be obtained, it must be presumed to be a *binary* one, unless some cause appear to the contrary. 2nd. When two combinations are observed, they must be presumed to be a *binary* and a *ternary*. 3rd. When three combinations are obtained, we may expect one to be a *binary*, and the other two *ternary*. 4th. When four combinations are observed, we should expect one *binary*, two *ternary*, and one *quaternary*, etc."

The following is Dalton's explanation of his use of the terms *binary, ternary*, etc.:

"If there are two bodies, A and B, which are disposed to combine, the following is the order in which the combinations may take place, beginning with the most simple, viz.:

   1 atom of A + 1 atom of B = 1 atom of C, binary.
   1 atom of A + 2 atoms of B = 1 atom of D, ternary.
   2 atoms of A + 1 atom of B = 1 atom of E, ternary.
   1 atom of A + 3 atoms of B = 1 atom of F, quaternary.
   3 atoms of A + 1 atom of B = 1 atom of G, quaternary, etc."

After giving some examples of the application of these rules to compounds of hydrogen and oxygen, of hydrogen and nitrogen, of nitrogen and oxygen, and of carbon and oxygen, Dal-

---

[1] Debus has published a pamphlet and some papers, dealing with the origin and development of Dalton's atomic theory. " Ueber einige Fundamental-Sätze der Chemie, insbesondere das Dalton-Avogadro'sche Gesetz," von Dr. Heinrich Debus [Cassel, 1894]. " Die Genesis von Dalton's Atomtheorie," von Heinrich Debus. *Zeitsch. für physikal. Chemie*, **20**, 359 [1895]; **24**, 325 [1897]; **29**, 266 [1899]. The last of these communications contains a recapitulation of the views of Debus.
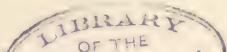
ton presents a table of the atomic weights of twenty elements (including, provisionally, baryta, lime, magnesia, potash, soda, and strontia) and seventeen compounds. The rest of the *New System* is concerned with descriptions of the elements and compounds, and contains the data which Dalton used to illustrate the applications of his theory, and on which he based values for the atomic weights of the various elements and compounds. At the end of Part III (published in 1827), Dalton gives values for the atomic weights of thirty seven elements, ten substances " simple or compound(?)," and many " compound elements."

Dalton very clearly stated that it is necessary to determine the number of atoms of an element which combine with other atoms to form compound atoms, before the atomic weight of the element in question can be found; at the same time he recognized that his theory did not furnish a general method for doing this which could be applied, simply and directly, to particular cases. In Part III of the *New System* (p. 350), he says that, to find the number of atoms of two substances, A and B, which combine, we must consider not only the compounds of A with B, but also the compounds of A with C, D, E, etc., and those of B with C, D, E, etc. And in another place (p. 207), he points out that the value 7, which he adopts for the atomic weight of oxygen, rests on the assumption that an atom of water is binary, that is, composed of one atom of hydrogen and one atom of oxygen, but that the atom of water may be ternary, and if it is ternary, then the atomic weight of oxygen will be either 14 or 3·5.[1]

This was the stumbling block in the application of Dalton's theory; several values were found for the atomic weight of an element, and the theory did not give a method for determining with certainty which of the possible values should be used. Dalton's rules were useful; but they were not much more than expressions of his personal preferences. Dalton's

---

[1] If the atom of water is binary, the formula for water will be HO, and the atomic weight of oxygen will be 7 (according to Dalton's data); but if the atom of water is ternary, the formula for water may be either H_2O (in which case O= 14), or HO_2 (in which case O= 3·5).

conception of the atom seemed definite, but his endeavours to apply that conception showed that it lacked precision. Some addition to the theory, or some modification of the theory, was required, such that a practical definition of the atom could be obtained. That practical definition followed upon Avogadro's recognition of two kinds of minute particles, the molecule and the atom. (See next chapter.)

Notwithstanding its incompleteness, Dalton's atomic theory was an immense help towards the solution of the two fundamental questions of chemistry; indeed it would not be an exaggeration to say that the most important advances made in chemistry since the publication of the *New System*, have been made by following lines of research suggested by applications of the atomic theory.

The additions which Dalton made to the ancient theory of the structure of material things, a theory which predicated differences in the sizes and weights of different kinds of atoms, were his demonstration of the possibility of determining the relative weights of the ultimate particles of elements and compounds, and the number of the atoms of the elements which constitute the ultimate particle of any compound, and his working out a method, although an incomplete method, for making these two determinations.

Before the publication of Dalton's *New System*, the atomic theory had done little more than enable men to represent some prominent properties of substances in a broad and general way. Dalton applied the theory to a special property, neither prominent nor striking, of certain classes of substances; the result was a mental picture in agreement with the facts. From that time the theory ceased to be an interesting speculation, and began to be a fine and powerful instrument of research.

The fundamental law of chemical composition, that all homogeneous substances react in the ratios of certain constant and determinable quantities by weight, or in the ratios of whole multiples of these quantities, was implied in the Daltonian theory of the structure of homogeneous substances. Although Dalton did not formulate this law he assumed the

accuracy of the atomic presentment of it at the very beginning of his work.[1] (Compare pp. 82, 83.)

This generalization has proved to be an accurate statement exactly applicable to every chemical change. But when Dalton announced an atomic theory of chemical change, wherein the accuracy of this law was implied, the experimental evidence in favour of the law was meagre and inexact. If the atomic theory was to be used as a means of classifying facts, and as an instrument for gaining new facts, a searching examination of the experimental foundations of the theory was required. Such an examination was made by several chemists, notably by Berzelius. It is interesting to observe that the work which followed the announcement of Dalton's theory did not directly aim at verifying, or disproving that theory, but was concerned with the experimental examination of the facts of chemical composition. The theory provided a motive for such investigations, and I have no doubt it was used by many chemists, certainly it was used by Dalton, as a criterion whereby the accuracy of their results might be judged.

In the year 1808, the year of the publication of Part I of Dalton's *New System*, papers were read before the Royal Society by Thomas Thomson and by W. H. Wollaston, on various salts of the same acid and base. Thomson[2] analyzed two oxalates of potash and two of strontia; in both pairs of salts he found that " the first contains just double the proportion of base contained in the second." Wollaston,[3] after referring to Thomson's results, says:

"As I had observed the same law to prevail in various other instances of super-acid and sub-acid salts, I thought it not unlikely that this law might obtain generally in such compounds, and it was my design to have pursued the subject with the hope of discovering the cause to which so regular a relation might be ascribed.   But since the publication of Mr. Dalton's theory of chemical combination, as explained and illustrated by Dr. Thomson,[4] the inquiry which I had designed appears to be superfluous, as all the facts

---

[1] I do not think that Dalton ever realized the law of multiple proportions as a generalized statement of facts, apart from a theory of the structure of elements and compounds.

[2] *Phil. Trans.*, **98**, 63 [1808].

[3] *Ibid.*, 96 [1808].

[4] The first published account of Dalton's views appeared in Thomson's *System of Chemistry*, 3d ed., vol. iii. pp. 424–9, 451–2 (Edinburgh, 1807). *Alembic Club Reprints*, No. 2 (1899), contains extracts from Thomson's *System of*

that I had observed are but particular instances of the more general observation of Mr. Dalton, that in all cases the simple elements of bodies are disposed to unite atom to atom singly, or, if either is in excess, it exceeds by a ratio to be expressed by some simple multiple of the number of its atoms."

Wollaston then describes experiments which show that the law—he speaks of it as the " law of simple multiples "—holds good for several pairs of salts of the same acid and base.

Johann Jacob Berzelius was born in East Gothland, Sweden, in August, 1779, five years after Priestley had obtained a new gas by heating *mercurius calcinatus;* he died in 1848. The first edition of his *Treatise on Chemistry* appeared (in Swedish) in 1807–8. In preparing that work, Berzelius tells us (for example, in *Théorie des Proportions chimiques*, Paris, 1835, 2d ed., p. 10), he read the memoirs of Richter on the compositions of salts (see pp. 74, 75), and determined to analyze a series of salts very carefully, in order to find the exact relations between the weights of acid and base which neutralized one another. While making these analyses he received *Nicholson's Journal* for November, 1808, which contained Wollaston's paper already referred to. Berzelius says that Wollaston's experiments arose from " the hypothesis of Dalton, that, when substances combine with one another in different proportions, these proportions always result from the simple multiplication of the weight of one of the substances by 1, 2, 3, 4, and so on." [1] Of this hypothesis, Berzelius says that if firmly supported by facts, it would be " the greatest advance chemistry had yet made towards its perfection as a science." Thereupon Berzelius began a more extended and systematic series of analyses of compounds. His earlier memoirs were published at Stockholm,[2] in the years 1810–11, and translations appeared in *Gilbert's Annalen* for 1811–12.[3]

Chemistry, also extracts from Thomson's paper in *Phil. Trans.*, and also Wollaston's paper " On Super-acid and Sub-acid salts."

[1] Translated from a paper by Berzelius, itself a translation from the original Swedish, in *Gilbert's Annal.*, **37**, 251, 2 [1811]. Compare Berzelius' statement with Wollaston's words quoted above. Berzelius does not use the word *atom*.

[2] *Afhandligar i Fysik, Kemi, och Mineralogi.*

[3] *Versuch die bestimmten und einfachen Verhältnisse aufzufinden, nach welchen die Bestandtheile der unorganischen Natur mit einander verbunden sind.* *Gilbert's Annal.*, **37**, 249, 415; **38**, 161, 227; **40**, 162, 235; **42**, 276, [1811–12]. Later volumes of *Gilbert's Annalen* contain many other memoirs by Berzelius on the compositions of salts. Some of the later memoirs were written in German by Berzelius himself.

In the first of these memoirs Berzelius says: "I do not
at all know how Dalton has developed his proposition, or on
what experiments he has based it; I cannot therefore judge
whether my experiments confirm this hypothesis entirely,
or whether they modify it more or less." The analyses made
by Berzelius in the years 1808–12 range over an immense field:
binary salts, such as chlorides, oxides, and sulphides; oxysalts,
such as sulphates, nitrates, and phosphates; hydrated salts;
acid salts; double salts; all are analyzed with consummate
skill, undaunted patience, and great accuracy. New methods
of analysis are tried, and used or rejected according to the
results obtained; many questions suggested by the results of
analyses are attacked by experimental methods devised to
suit the needs of each problem; these memoirs show that to
be a great analyst, a man must be also a great chemist.

Summing up his results in 1812, Berzelius said: [1]

"When two substances which we take to be simple, combine in several
proportions, then, taking the quantity of the electronegative substance
as constant, these proportions are multiples, by $1\frac{1}{2}$, 2, 4, and so on, of the
smallest proportion in which the electropositive substance can combine
with the electronegative." [2]

The *law of multiple proportions* was thus established by
Berzelius, for many compounds, about the year 1812. Dal-
ton had assumed the law, and the universality of its appli-
cation, in his general theory of chemical combination. Ber-
zelius, incited thereto by one of the hypotheses implied in
Dalton's theory, confirmed the accuracy of the law, for many
compounds, by a series of accurate analyses.

The methods of these two naturalists were very different.
In a letter (written in German) to Gilbert,[3] dated Stockholm,
May 12th, 1812, Berzelius says he has at last received Dalton's
book, and is astonished: "Ich wartete darin zu erfahren,

[1] *Gilbert's Annal.*, **40**, 320.
[2] In a note Gilbert pointed out that this statement did not express what
Berzelius meant. Gilbert proposed to amend the statement thus: "If two
substances, an electronegative A, and an electropositive B, combine with one
another in different proportions, for example, m parts by weight of A with n,
or with n', or with n'', or with n''', parts by weight of B, the numbers n, n',
n', n'', etc., are in the proportion of $1 : 1\frac{1}{2} : 2 : 4$, etc.; or (with the exception
of $1\frac{1}{2}$) n is an *aliquot part* of the other numbers, and these numbers are whole
multiples of n."
[3] *Gilbert's Annal.*, **42**, 274.

wie Dalton mit denselben Schwierigkeiten kampfend als ich,
sie vielleicht siegreicher überwunden habe!'' Berzelius laid
a broad foundation of facts, and then generalized cautiously.
Referring to certain facts which seemed to be well established
by experiment,[1] Dalton [2] said: '' No principle has yet been
suggested to account for the phenomena; till that is done I
think we ought to investigate the facts with great care, and
not suffer ourselves to be led to adopt these analyses till
some reason can be discovered for them.''

The field opened by Berzelius found many cultivators. The
establishment of the *law of multiples* on a basis of facts, inde-
pendently of any theory of the structure of homogeneous sub-
stances, suggested that the compositions of many compounds
might be expressed by using that law only. In his *System of
Chemistry*, Thomson [3] gave the weights of various acids and
bases that neutralized one another, saying that these numbers
were ''independent of the hypothesis of Dalton.'' In his
Elements of Chemical Philosophy, Davy (in 1812) stated the
laws of chemical combination, and then gave a very brief ac-
count of the atomic theory. Wollaston [4] (in 1814) deduced
the *equivalent weights* of twelve elements and forty five com-
pounds from the analyses, mostly made by other chemists, of
many compounds. Wollaston wished to find the quantities of
various elements and compounds which actually combined, and
the quantities of the products of these combinations; ''prac-
tical convenience'' was his ''sole guide.'' He thought that the
term *equivalent weight* was less theoretical than *atomic weight*.
In order to make his results easily used by analysts, Wollaston
invented an instrument called a ''*Logometric* scale of chemical
equivalents adapted for experimental and manufacturing
chemists.'' [5]

---

[1] The combinations of gases in equal and multiple volumes.
[2] *New System.* Appendix to Part III, p. 349.
[3] Fourth edition, 1810, pp. 630, 631.
[4] *Phil. Trans.* for 1814 (Part I), p. 1.
[5] The instrument consists of a flat piece of wood, the central part of which
is movable; the names of many elements and compounds are marked on either
side of the slide, with a number attached to each. The number on the slide express-
ing the weight taken of one of two reacting substances is placed opposite the
name of that substance, and the number now found opposite the name of the
other reacting substance, on the fixed part of the instrument, expresses the

The progress of the work on the compositions of compounds, during the twenty or twenty five years after the publication of Dalton's *New System,* is best followed by examining the first German edition of Berzelius' *Lehrbuch der Chemie* (translated by Wöhler, 1825–1831). In the third volume of that book (p. 31), Berzelius says that the particles of substances which combine may be called atoms, molecules, particles, chemical equivalents, etc.; he prefers the term *atom,* because it expresses more correctly than any other the idea he wishes to convey.[1] In considering the proportions wherein atoms combine, Berzelius said (pp. 35–43 of vol. iii) that most of the compounds of two elements are composed either of one atom of one of the elements with one, two, three, four, etc., atoms of the other element (the maximum number of atoms of the second element being unknown), or of two atoms of one of the elements with three or five atoms of the other element. Berzelius was not able to give a final answer to the question, Do compound atoms exist composed of two atoms of one element with two of another, or with four or six atoms of another element, which cannot consist of a single atom of the first element combined with one, or with two, or three atoms of the second element? For instance, taking water to be a compound of two atoms of hydrogen with one atom of oxygen, must peroxide of hydrogen be expressed by the formula H_2O_2, or may the formula HO be used?

Regarding the combinations of compound atoms, Berzelius said that the commonest case was the union of a single compound atom with one, two, three, etc., other compound atoms, but that three compound atoms of one kind sometimes combined with two, or (very seldom) with three, or four, compound atoms

---

weight of that substance which reacts. Opposite the name of the product of the reaction is also found a number which tells the weight of that product. This instrument is referred to by Thomson in the fifth edition of his *System of Chemistry* (1817, vol. iii. p. 18), as Wollaston's " Sliding rule of chemical equivalents so precious in every point of view to the practical chemist."

[1] So far as I know, Thomas Young was the first to use the expression *combining weight.* Young's *Introduction to Medical Literature* (published in 1813) contains a section headed " Chemistry," and in that section there is a table entitled " Properties of peculiar substances," which gives the specific gravity and other properties of each element; a number is attached to each element, and the column containing these numbers is headed *Weight combining.*

of another kind, and sometimes five compound atoms of one kind united with two, three, four, etc., of another kind.

The surest method, although a method of limited applicability, for determining the relative numbers of simple atoms in the atom of a compound was said by Berzelius to be the determination of the volumes of elementary gases which combined; because the weights of the atoms and the weights of the combining volumes of elementary substances were identical.[1] (See pp. 115, 116.) In the cases of oxides, the relations between the numbers of combining atoms were said by Berzelius to be 1:2 or 2:4, 1:3 or 2:6, etc.; analogy, he added, was the main guide. In dealing with the combinations of electropositive and electronegative oxides (basic and acidic oxides, we should call them now), Berzelius laid down the rule that the quantity of oxygen in the negative oxide was a whole multiple of the quantity of oxygen in the positive oxide, and the multiple was generally equal to the number of atoms of oxygen in the negative oxide.[2]

In later editions of his *Lehrbuch*, Berzelius developed these methods, and applied them to the determination of the atomic weights of very many elements.

The work of chemists who studied the compositions of compounds immediately after the publication of Dalton's *New System* was concerned chiefly with the establishment, on a sound experimental basis, of the law of composition, taken for granted in Dalton's atomic theory, that all homogeneous substances react in the ratios of certain constant and determinable quantities by weight, or in the ratios of whole multiples of these quantities. As that law was being established, attempts were constantly made to determine values for the combining weights of the elements, and to express the compositions of compounds in terms of these constant quantities: the work done in this direction followed closely the lines laid down by Dalton; and

---

[1] Berzelius applied the generalization, *equal volumes contain equal numbers of atoms*, only to elements, and only to those elements which are gases at the ordinary temperature and pressure.

[2] Berzelius also used the *law of specific heats*, and the *law of isomorphism*, as helps in finding the numbers of atoms that combine to form more complex atoms. (The history of these laws is considered on pp. 116–124).

most chemists used the nomenclature introduced by Dalton, and spoke of the *atomic* weights of elements and the weights of the *atoms* of compounds. But the difficulty so clearly recognized by Dalton was not overcome. No general principle was found by Berzelius, as none had been found by Dalton, which was directly applicable to every case, and decided the value to be assigned to the atomic weight of the element under consideration, by deciding the number of simple atoms in the atoms of compounds of that element, and the relative weights of these compound atoms.

The difficulty was removed by amplifying and extending the theory of Dalton; not by merely accumulating experimental details. The amplification of the Daltonian theory will be considered in the next chapter. At present I ask the reader's attention to the work of Stas on the laws of chemical combination.

In a series of memoirs published from 1840 to 1882, Stas proved conclusively that the *laws of chemical combination* are rigorously accurate expressions of facts, and are exactly applicable to all chemical reactions.[1]

In order to determine whether the composition of a compound is constant, Stas prepared ammonium chloride by saturating a solution of ammonia with pure hydrochloric acid gas, evaporating, drying the salt at 100°, and subliming in an atmosphere of ammonia. Three specimens of ammonium chloride were prepared from three solutions of ammonia: the first of these solutions was obtained by heating, with lime, ammonium chloride which had been purified by boiling with *aqua regia*, and leading the gas into water; the second was obtained by heating, with lime, ammonium sulphate which had been purified by boiling with sulphuric acid and a little nitric acid, and leading the gas into water; and the third solution was obtained by

---

[1] Jean-Jervais Stas, born at Louvain in 1813, died at Brussels in 1891. His most important memoirs on chemical composition are: (1) *Recherches sur les rapports réciproques des poids atomiques* (*Bull. de l'Acad. royale de Belgique* for 1860); and (2) *Nouvelles recherches sur les lois des proportions chimiques, sur les poids atomiques et leurs rapports mutuels* (*Mém. de l'Acad. royale de Belgique* for 1865). A translation into German (by Aronstein) of these two memoirs (the first memoir somewhat abbreviated) appeared in 1867, with the title *Untersuchungen über die Gesetze der Chemischen Proportionen über die Atomgewichte und ihre gegenseitigen Verhältnisse.* [Leipzig, Quandt and Händel.]

leading into water the ammonia formed by reducing, by zinc and iron, a solution of potassium nitrite prepared by heating potassium nitrate with lead. A portion of the third specimen of ammonium chloride was sublimed under the pressure of about half a millimetre of mercury. Weighed quantities of each of the four specimens of ammonium chloride were caused to react, in solution, with weighed quantities of pure silver, dissolved in nitric acid; the precipitated silver chloride was weighed, and the silver that remained in solution was determined by titration with a solution of pure sodium chloride of known strength. Elaborate precautions were taken in the purification of all the materials used.

The results of these experiments proved conclusively that the ratio of the weights of ammonium chloride and silver which react in solution is absolutely constant, that the composition of ammonium chloride is not affected by changes of temperature or pressure, and that change of temperature does not alter the composition of silver chloride.

That the accuracy of the law of constant proportions should be proved, Stas said it was necessary to change several ternary compounds, ABC, into binary compounds, AB, by removing the element C without the expulsion of any trace of A or of B, and to prove the ratio of the weights of A and B in one compound to be identical with the ratio of the weights of these elements in the other compound. He selected the compounds silver iodate, silver bromate, and silver chlorate, because he found it was possible, although exceedingly difficult, to prepare these compounds pure, to reduce them to silver iodide, bromide, and chloride (by the reaction of sulphur dioxide in presence of water), without the loss of the minutest trace of iodine, bromine, or chlorine, and because of the great accuracy of the methods which he had perfected for estimating silver, iodine, bromine, and chlorine.

The results of many experiments, conducted with a patience, care, and accuracy that are almost appalling, proved that the ratio of the weights of silver and iodine in silver iodate is identical with the ratio of the weights of the same elements in silver iodide, the ratio of the weights of silver and bromine in

silver bromate is identical with the ratio of the weights of the same elements in silver bromide, and the ratio of the weights of silver and chlorine in silver chlorate is identical with the ratio of the weights of the same elements in silver chloride.

Stas concluded that the weights of homogeneous substances which react bear an absolutely constant proportion to one another, and that the laws of chemical combination are mathematically accurate expressions of facts.

That he might obtain confirmation of his conclusion that the elements combine, under normal conditions, exactly in the ratios of certain fixed quantities by weight, Stas determined (I) the ratio between the weights of silver and iodine which combine to form silver iodide, and the ratio between the weights of silver iodide and oxygen obtained from silver iodate; (II) the ratio between the weights of silver and bromine which combine to form silver bromide, and the ratio between the weights of silver bromide and oxygen obtained from silver bromate; (III) the ratio between the weights of silver and chlorine which combine to form silver chloride, and the ratio between the weights of silver chloride and oxygen obtained from silver chlorate. By stating his results in another form, the data obtained gave (I) the weights of silver iodide, silver bromide, and silver chloride, respectively, combined with one and the same weight of oxygen—Stas took this fixed weight of oxygen as 3×16; (II) the weights of silver combined with this fixed weight of oxygen, in three different compounds; and (III) the several weights of iodine, bromine, and chlorine combined with this fixed weight of oxygen.

The following is a statement of Stas' final results.

I. *Weight of silver combined with* 3×16 *parts by weight of oxygen.*

	I.	II.	III.	Mean.
From syntheses of silver iodide, and analyses of silver iodate.........	107·918	107·950	107·917	107·928
From syntheses of silver bromide, and analyses of silver bromate........	107·905	107·937	....	107·921
From syntheses of silver chloride, and analyses of silver chlorate........	107·929	107·947	....	107·937

II. *Weights of iodine, bromine, and chlorine, severally combined with* 3×16 *parts by weight of oxygen.*

<table>
<tr><td></td><td>Mean.</td></tr>
<tr><td>A. <i>Iodine;</i> from syntheses of silver iodide, and analyses of silver iodate. ....</td><td>126·857</td></tr>
<tr><td>B. <i>Bromine;</i> from syntheses of silver bromide, and analyses of silver bromate. ....</td><td>79·940</td></tr>
<tr><td>C. <i>Chlorine;</i> from syntheses of silver chloride, and analyses of silver chlorate ....</td><td>35·458</td></tr>
</table>

Stas conducted his experiments with the most extraordinary care; nevertheless experimental errors were unavoidable. Considering that the numbers from which the mean results given above were obtained showed almost equal divergences from the mean values, Stas concluded that the values obtained for what may be called the combining weight of silver are identical, and that the combining weights of chlorine, bromine, and iodine are unchangeable quantities.

The following numbers taken from Stas' memoir illustrate his experimental results. All weighings are in grams and are reduced to weighings *in vacuo.*

I. *Syntheses of silver iodide.*

Weight of iodine.	Weight of silver.	Sum of weights of silver and iodine.	Weight of silver iodide obtained.
32·4665	27·6223	60·0888	60·086
44·7599	38·0795	82·8394	82·8375
160·2752	136·3547	296·6299	296·6240

Ratio of weights of silver and iodine combined (silver = 100).

(I) from weights taken	(II) from weights obtained.
117·539	117·529
117·543	117·539
117·542	117·538

II. *Analyses of silver iodate.*

Weight of silver iodate.	Weight of silver iodide.	Weight of oxygen.	Sum of weights in cols. 2 and 3.	Difference between numbers in cols. 1 and 4.
156·7859	130·1755	26·6084	156·7839	−·002
98·2681	81·5880	16·6815	98·2695	+·0014

Taking the mean results of three analyses of silver iodate, the percentage composition of this salt is found to be:

Silver iodide, 83·0253
Oxygen,   16·9747.

Combining this with the mean result of six syntheses of silver iodide, it is found that

107·928 parts by weight of silver, and 126·857 parts by weight of iodine, combine with 3×16 parts by weight of oxygen.

The rest of the work of Stas is concerned chiefly with determinations of the combining weights (he generally uses the term atomic weight) of certain selected elements, his main purpose being a critical examination of the hypothesis that the atomic weights of many elements bear a simple relation to the atomic weight of hydrogen.[1] The methods used by Stas in dealing with his experimental results depended on the accuracy of the laws of chemical combination, and the results he obtained confirmed the accuracy of these laws.   The labours of this great chemist—the most patient, the most undaunted, the most careful, and the wisest of experimentalists—proved conclusively that the law of constant proportions, the law of multiple proportions, and the law of reciprocal proportions, are mathematically accurate expressions of facts which hold good throughout the whole range of chemical interactions.[2]   In doing this, Stas also strengthened the foundation of the atomic theory; for, as he says, the only solid basis of that theory is the actual, and not merely the virtual constancy of composition of compounds, and the actual constancy of the relations between the combining weights of the elements.[3]

The account I have given in this chapter of the study of the composition of homogeneous substances, after the time of Lavoisier, shows how closely the enunciation of the laws of chemical composition, as descriptions of facts, was intermingled with the theoretic presentment of these laws in terms of the atomic theory. For the clearer understanding of the next stages in the advance in the knowledge of composition, it is advisable now to disentangle the laws and the theoretic presentment of them.

It is customary to express the facts concerning the masses which react of elements and compounds, in three statements.

---

[1] This hypothesis will be referred to in Chapter XII.

[2] Stas' results incidentally confirmed the accuracy of the law of the conservation of mass, which states that the sum of the masses of the products of any reaction between homogeneous substances is equal to the sum of the masses of the reacting substances.   This law was also confirmed by the results of a series of measurements made by Landolt in 1893.   (*Zeitsch. für physikal. Chemie*, **12**, 1.)

[3] A more detailed account of the experiments of Stas is given in Miss Freund's *The Study of Chemical Composition*, pp. 65–72 [1904].

I. *Law of constant proportions.* The masses of the constituent elements of every compound stand in an unchangeable proportion to each other and also to the mass of the compound.

II. *Law of multiple proportions.* The different masses of an element or of a compound which combine or react with one and the same mass of another homogeneous substance, can be expressed as whole multiples of the smallest of these masses.

III. *Law of reciprocal proportions.* The proportion between the masses of different elements and compounds which combine or react with one and the same mass of another homogeneous substance, is also the proportion, or it bears a simple relation to the proportion between the masses of the different elements and compounds which combine or react with each other.

These three laws may be expressed in one statement.

To every homogeneous substance can be assigned a certain number, expressing a definite mass of that substance, which may be called its combining weight, or its reacting weight; all chemical reactions between elements and compounds occur between masses of them which can be expressed by the numbers in question, or by whole multiples of these numbers.

The work which has been summarized in this chapter, and similar investigations by many chemists whom I have not mentioned, made fuller and clearer the answer to be given to the question, What is a homogeneous substance? An element was now a homogeneous substance, not divisible by any available method, which always interacts chemically in quantities by weight expressed by its combining weight, or by whole multiples thereof. A compound was now a homogeneous substance which always interacts chemically in quantities by weight expressed by its reacting weight, or by whole multiples thereof, and is formed by the union of, and is divisible into such quantities by weight of two or more elements as are expressible by the combining weights, or by whole multiples of the combining weights of these elements.

The second question of chemistry, What happens when homogeneous substances interact? was also more fully answered by the investigations summarized in this chapter. A chemical reaction was now the formation of a compound by the union of

definite quantities of certain elements, or the resolution of a compound into definite quantities of certain elements, or the resolution of several compounds into definite quantities of certain elements, and the formation of a new compound, or new compounds, by the redistribution of these elements; the quantities by weight of the interacting compounds, and of the elements produced, or combined, or redistributed, being always proportional to the reacting weights, and the combining weights, of the compounds an the elements.

The mental picture which the atomic theory provided of the facts of chemical combination might be described by repeating the foregoing statements, with the substitution of the expression *atomic weight* for the expressions *combining weight* and *reacting weight*.

But the answers to the two fundamental questions of chemistry were not yet sufficiently clear, full, and suggestive; nor was the atomic presentment of the answers complete. The purpose of the following chapter is to trace the next stages in the elucidation of the facts, and of the theory.

CHAPTER IV.

THE DIFFERENTIATION OF THE ATOM AND THE MOLECULE. THE DETERMINATION OF ATOMIC AND MOLECULAR WEIGHTS.

ELEMENTS and compounds react chemically in the ratios of their combining or reacting weights, or in the ratios of whole multiples of these weights; or, using the language of the Daltonian atomic theory, elements and compounds react in the ratios of their atomic weights, or of whole multiples of these weights. The laws of chemical combination, and the Daltonian theory, carry us as far as this; but neither from these laws nor from that theory can a general method be deduced for determining which of several possible values of the combining weight, or of the atomic weight of an element is to be chosen, or for selecting *the* value of the reacting weight of a compound, or of the weight of a compound atom, from the several possible values.

The difficulty may be stated in a slightly different form. Berzelius proposed a question to which the Daltonian theory could not give a final answer: Do compound atoms exist composed of two atoms of one element with two, or with four or six atoms of another element, which cannot consist of a single atom of the first element combined with one, or with two or three atoms of the second element? (See p. 92.) And if it was sought to represent the compositions of compounds on the basis of the laws of combination alone, without the help of the Daltonian theory, what was practically the same question stopped the way. Thus, in his *Elements of Chemistry* (6th ed., 1835), Turner regarded water as a compound of one equivalent weight of hydrogen and one equivalent weight of oxygen (he preferred to speak of equivalent weights rather than atomic weights), and therefore he gave the value 8 to the equivalent

weight of oxygen. That he may find the equivalent weights of other elements, "The chemist," said Turner (p. 221), "then selects for analysis such compounds as he believes to contain one equivalent of each element, in which either oxygen or hydrogen, but not both, is present." But on what grounds was the chemist to found his *belief* that this or that compound contained one equivalent of oxygen or one equivalent of hydrogen? On such grounds as these: "Metallic oxides, distinguished for strong alkalinity, . . . are always protoxides. Dioxides rarely unite definitely with acids, and are remarkable for their ready conversion into protoxides, with separation of metal." We have here the Daltonian maxims, the Berzelian rules, in another form. Each case had to be discussed more or less by itself. Before the most suitable value was selected for the atomic weight (or the combining or reacting weight) of an element or of a compound, the chemical similarities between that element and many other elements, or between that compound and many other compounds, had to be examined minutely, and in that examination analogy was the chief guide.

If the study of composition and reactions was to advance, it was necessary to find a general principle capable of supplying a method of selecting the most suitable value for the combining weight, or the atomic weight, of any element or compound.

The material for the construction of such a general principle was supplied in a memoir by Avogadro, published three years after the appearance of Part I. of Dalton's *New System of Chemical Philosophy;* but nearly half a century passed before the great advance made in that memoir was realized by chemists.

Before considering the work of Avogadro, we must go back to the year 1809, and to a paper published in that year by Gay-Lussac, with the title *Mémoire sur la combinaison des substances gazeuses, les unes avec les autres.*[1]

"I have shown in this memoir," Gay-Lussac said in summarizing his results, "that the compounds of gaseous substances with each other are always formed in very simple ratios, so that representing one of the terms by unity, the other is 1, or 2, or at most 3. . . . The apparent contraction of volume

---

[1] *Mém. de la Soc. d'Arcueil,* II (1809), p. 207. A translation of this paper was published in 1899 as No. 4 of *Alembic Club Reprints;* the quotations in the text are from that translation.

suffered by gases on combination is also very simply related to the volume of one of them."

Gay-Lussac said that the properties of gases which are expressed in the words I have quoted are in keeping with other properties of gases, such as their equal dilatation by heat and equal diminution of volume by pressure; he regarded the relations between the combining volumes of gases as "a new proof that it is only in the gaseous state that substances are in the same circumstances and obey regular laws."

The following is a summary of the evidence whereon Gay-Lussac rested his conclusions. Equal volumes of fluoboric acid [1] and ammonia, muriatic acid and ammonia, and carbonic acid and ammonia, combine to form neutral salts; fluoboric acid and carbonic acid also combine with twice their volume of ammonia to form *sub-salts*. Sulphurous acid gas combines with half its volume of oxygen to form sulphuric acid, and carbonic oxide combines with half its volume of oxygen to form carbonic acid. Gay-Lussac referred to experiments made by Humboldt and himself, according to which hydrogen combines with half its volume of oxygen to form water,[2] and to experiments of A. Berthollet which gave the ratio of the volumes of nitrogen and hydrogen that form ammonia as 1:3. In no case does Gay-Lussac give details of his experiments.

Taking Davy's analyses of three oxides of nitrogen, and "reducing these proportions to volumes," he obtained these results:

	Nitrogen.	Oxygen.
Nitrous oxide.	100	49·5
Nitrous gas.	100	108·9
Nitric acid.	100	204·7

Gay-Lussac took the first and last of these ratios as 100:50 and 100:200, respectively: with regard to nitrous gas (nitric oxide) he said he had himself burned "the new combustible substance from potash" in 100 volumes of this gas and obtained exactly 50 volumes of nitrogen. His experiments with chlorine led to a result which now seems extraordinary, namely, that oxygenated muriatic acid (that is, chlorine) is composed of

---

[1] From the method of its preparation, Gay-Lussac's fluoboric acid was evidently *boron trifluoride*.

[2] *Journal de Physique*, **60**, 129 (1805).

muriatic acid and oxygen in the ratio of $3:1$ by volume. As regards the volumes of the products of the combinations of gases, Gay-Lussac said that the volume of carbonic acid formed by burning carbonic oxide in oxygen is the same as the volume of carbonic oxide burned, that the contraction which occurs when two volumes of nitrogen combine with one volume of oxygen to form nitrous oxide is equal to the volume of the oxygen, that there is no contraction in the formation of nitric oxide, that the contraction when hydrogen and oxygen combine to form water is equal to the volume of the oxygen, and that when nitrogen and hydrogen form ammonia the contraction is equal to half the total volume of the combining gases. Most of these conclusions are based on the determinations, made by different chemists, of the specific gravities of the various gases, and of the products of their combination.

Although more accurate measurements than were possible at the time of Gay-Lussac, made with very much purer gases than could be prepared then, have justified Gay-Lussac's general conclusions and confirmed most of the special results whereon he rested these conclusions, we recognize that Dalton was warranted in speaking of Gay-Lussac's "*hypothesis* that all elastic fluids combine in . . . measures that have some simple relation one to another," in criticising Gay-Lussac's experiments, and in claiming consideration for his own results which led him to think that "gases do not unite in equal or exact measures in any one instance; when they appear to do so, it is owing to the inaccuracy of our experiments."[1]

Writing of Gay-Lussac's generalization, Dalton said (*l. c.*):

"In fact, his notion of measures is analogous to mine of atoms; and if it could be proved that all elastic fluids have the same number of atoms in the same volume, or numbers that are as 1, 2, 3, etc., the two hypotheses would be the same, except that mine is universal, and his applies only to elastic fluids. Gay-Lussac could not but see (p. 188, Part I of this work) that a similar hypothesis had been entertained by me, and abandoned as untenable."

---

[1] Part II of *A New System of Chemical Philosophy* (1810), Appendix, pp. 555–559. (Italics are mine.) Dalton finds fault with Gay-Lussac's account of his experiments on burning potassium in nitrous gas: "The degree of purity of the nitrous gas and the particulars of the experiment are not mentioned. This one result is to stand against the mean of three experiments by Davy, and may or may not be more correct, as hereafter shall appear."

That the Daltonian notion of the atom did not make it necessary to read into Gay-Lussac's generalization the hypothesis that equal volumes of gases contain equal numbers of atoms, is evident from Dalton's own words (*New System*, Part I pp., 70, 71): "If equal measures of azotic and oxygenous gases were mixed, and could be instantly united chemically, they would form nearly two measures of nitrous gas [nitric oxide], having the same weight as the two original measures; but the number of ultimate particles could at most be one-half of that before the union."

The only difference between Dalton and Gay-Lussac, so far as the actual facts were concerned in this case, was that Gay-Lussac said that one volume of oxygen combines with one volume of nitrogen to produce two volumes of nitrous gas, and Dalton said that the product measures nearly two volumes. As regards numbers of atoms, Dalton assumed that a determinate volume of nitrogen contains the same number of atoms as an equal volume of oxygen, and the same number as is contained in about twice that volume of nitrous gas; for he represented an atom of nitrous gas to be composed of one atom of nitrogen with one atom of oxygen, and he said that nitrous gas was formed by the union of equal volumes of nitrogen and oxygen; but at the same time, Dalton supposed Gay-Lussac to conclude that equal volumes of the three gases in question contained the same number of atoms.

If the weights of those volumes of gases which combine were determined, Gay-Lussac's generalization might be stated thus: the weights of gaseous elements and compounds which react bear simple relations to each other; these weights can always be expressed, for each reacting gas, as whole multiples of a certain fixed weight. This is merely an extension of the law of multiple proportions, the enunciation whereof has generally been assigned to Dalton. The refusal of Dalton to accept the generalization of Gay-Lussac seems to confirm what I have said (see note, p. 88), that he probably never realized the law of multiple proportions as a statement of facts apart from his atomic theory, and to show that it was almost impossible for him to think about chemical occurrences except as

transactions between atoms of different weights and different sizes.

It must be admitted that Dalton's rendering of Gay-Lussac's generalization was the simplest and most probable re-statement thereof that could be made in terms of the atomic theory, and that, admitting the justness of Dalton's rendering, either Gay-Lussac's facts were inaccurate, or the Daltonian conception of the atom required modification.

Avogadro's memoir was published in 1811; it was entitled, *Essai d'une manière de déterminer les masses rélatives des molécules élémentaires des corps, et les proportions selon lesquelles elles entrent dans les combinaisons.*[1]

Avogadro admitted the atomic presentment of the facts of combination, namely, that the proportions between the quantities of the constituents of compounds are dependent on the relative numbers of the particles of these constituents and the number of compound particles formed; he also admitted the generalization of Gay-Lussac, that there is a simple relation between the volumes of gases which combine, and also between these volumes and those of the gaseous products. These admissions led Avogadro to the conclusion that "the number of molecules in any gases is always the same for equal volumes," because, on any other hypothesis, "it would scarcely be possible to conceive that the law regulating the distance of particles could give us in all cases relations so simple as those which the facts [announced by Gay-Lussac] compel us to acknowledge between the volume and the number of particles."[2]

---

[1] By Amedeo Avogadro (born 1776, died 1856); *Journal de physique de Delaméthrie*, **73**, pp. 58–76. A translation was published in 1899 in No. 4 of *Alembic Club Reprints*; the quotations in the text are from that translation, except that I have altered the English equivalents of some of Avogadro's terms (see next note).

[2] Avogadro uses the word *molécule* either alone or with one or other of three qualifying adjectives. *Molécule* is used as synonymous with both the modern terms *atom* and *molecule*; I have rendered this term by "particle," and in quotations from the Alembic Club's translation I have ventured to substitute " particle " for the translator's " molecule." *Moélcule constituante* means, in modern nomenclature, *molecule* of an element; *molécule integrante* (an expression used by Lavoisier) means *molecule*, and is generally applied by Avogadro to compounds; the Alembic Club's translation renders these terms by " constituent molecule," and " integral molecule," respectively. I have preferred to render them both by " molecule," and here, again, I have ventured to alter the translation when I quote from it. *Molécule élémentaire* is translated " elementary

"Setting out from this hypothesis," Avogadro said, "it is apparent that we have the means of determining very easily the relative masses of the particles of substances obtainable in the gaseous state, and the relative number of these particles in compounds; for the ratios of the masses of the particles are then the same as those of the densities of the different gases at equal temperature and pressure, and the relative number of particles in a compound is given at once by the ratio of the volumes of the gases that form it. For example, since the numbers 1·10359 and 0·07321 express the densities of the two gases oxygen and hydrogen compared to that of atmospheric air as unity, and the ratio of the two numbers consequently represents the ratio between the masses of equal volumes of these two gases, it will also represent, on our hypothesis, the ratio of the masses of their particles. Thus the mass of the particle of oxygen will be about 15 times that of the particle of hydrogen, or, more exactly, as 15·074 to 1. . . . On the other hand, since we know that the ratio of the volumes of hydrogen and oxygen in the formation of water is 2 to 1, it follows that water results from the union of each particle of oxygen with two particles of hydrogen."

Avogadro then states the difficulty which seemed to prevent the application of his hypothesis to compounds:

" . . . if in a compound one particle of one substance unites with two or more particles of another substance, the number of compound particles should remain the same as the number of particles of the first substance. Accordingly, on our hypothesis, when a gas combines with two or more times its volume of another gas, the resulting compound, if gaseous, must have a volume equal to that of the first of these gases. Now, in general, this is not actually the case."

To remove this difficulty, Avogadro says:

"We suppose that the molecules of any simple gas whatever (that is, the particles which are at such a distance from each other that they cannot exercise their mutual action) are not formed of a solitary atom, but are made up of a certain number of these atoms united by attraction to form a single [molecule]; and, further, that when particles of another substance unite with the former to produce a compound particle, the molecule which should result splits up into two or more parts [or molecules] composed of half, quarter, etc., the number of atoms going to form the molecule of the first substance, combined with half, quarter, etc., the number of molecules of the second substance that ought to enter into combination with one molecule of the first subsatnce; . . . so that the number of molecules of the compound becomes double, quadruple, etc., what it would have been if there had been no splitting up, and exactly what is necessary to satisfy the volume of the resulting gas. Thus, for example, the molecule of water will be composed of a half molecule of oxygen with one molecule, or, what is the same thing, two half-molecules of hydrogen."

molecule " in the Alembic Club's pamphlet; as Avogadro uses this term to mean what we now call an atom, I have made bold to substitute " atom " for " elementary molecule " in quotations from the translation in question.

One of Avogadro's arguments in favour of the possibility of the division of molecules illustrates that mental tendency to impose our own standard of simplicity on natural events which has greatly hindered the advance of accurate knowledge.

"The possibility of this division of compound particles," he says, "might have been conjectured *a priori;* for otherwise the molecules of bodies composed of several substances with a relatively large number of particles would come to have a mass excessive in comparison with the molecules of simple substances. We might, therefore, imagine that nature had some means of bringing them back to the order of the latter, and the facts have pointed out to us the existence of such means."

Avogadro compared his hypothesis with that of Dalton:

"On arbitrary assumptions as to the most likely relative number of particles in compounds, Dalton has endeavoured to fix ratios between the masses of the particles of simple substances. Our hypothesis, supposing it well-founded, puts us in a position to confirm or rectify his results from precise data, and, above all, to assign the magnitude of compound particles according to the volumes of the gaseous compounds, which depend partly on the division of particles entirely unsuspected by this physicist." And again: " . . . our hypothesis . . . is at bottom merely Dalton's system furnished with a new means of precision from the connexion we have found between it and the general fact established by M. Gay-Lussac."

Avogadro states very definitely that, in order to find the molecular weight of an element or compound, it is necessary to determine the density of the substance in the state of gas, and to refer this to the density of hydrogen taken as unity. He discusses several cases. Let us glance at his treatment of hydrochloric acid or muriatic acid as it was then called.

The experiments of Davy had convinced Avogadro that the substance then known as oxymuriatic acid was an element, and muriatic acid was a compound of that element with hydrogen. Dividing the density of oxymuriatic acid gas [chlorine] by that of hydrogen (both referred to air as unity), he obtained the quotient 33·74; and from other data (those of Davy) he obtained the quotient 32·82. Hence he concluded that the molecular weight of oxymuriatic acid was about 33, referred to that of hydrogen as unity. Experiments had shown that equal volumes of oxymuriatic acid and hydrogen combined to form a volume of muriatic acid equal to the sum of the volumes of its constituents. "This means," said Avogadro, "according to our

hypothesis, that muriatic acid is formed of these two sub-
stances united particle to particle, with halving of the par-
ticles of which we have already had so many examples."
These results showed that the molecular weight of muriatic
acid, referred to the molecular weight of hydrogen as unity,
was about $\frac{33+1}{2} = 17$. The value 17·18 was found for the
molecular weight of this gas by dividing the density of it, deter-
mined by Davy, by the density of hydrogen.

As the data regarding the densities of gases were scanty
and not very accurate at the time of Avogadro, he was able to
make direct application of his method of finding the relative
weights of the ultimate particles of substances to but a small
number of elements and compounds.[1]

Avogadro tried to calculate various molecular weights by
the method of analogy, supplemented by the application of his
hypothesis to data concerning the relative densities of sub-
stances from which those he was examining could be formed.
His calculation of the molecular weight of gaseous sulphur
may be taken as an example of these attempts. He arrived at
the composition of sulphurous acid [sulphur dioxide] from de-
terminations of its density, from analyses of sulphuric acid [sul-
phur trioxide], and from measurements of the volumes of sul-
phurous acid and oxygen which combined to form sulphuric acid.

"Analogy with other combinations already discussed, where there is in
general a doubling of the volume or halving of the molecule, leads us to
suppose that it is the same in this case also [the formation of sulphurous
acid from sulphur and oxygen], that is, that the volume of the sulphur gas
is half that of the sulphurous acid, and consequently also half that of the
oxygen with which it combines."

Considering this conclusion along with the composition of
sulphurous acid, he inferred that the ratio between the   ties

<hr>

[1] The molecular weights of three elements and of six compounds   calcu-
lated in Avogadro's memoir directly from the values of the relative   ensities
of these gases given by various authorities. The elements are oxygen, nitrogen,
and chlorine. Avogadro's values for the three molecular weights are, approxi-
mately, 15, 13, and 33. The compounds are water (molecular weight about
8·5), ammonia (m.w. about 8), hydrochloric acid (m.w. about 17), nitrous oxide
(m.w. about 20·7), nitric oxide (m.w. about 14), and nitrogen dioxide (m.w.
about 21·5). These values are all referred to the molecular weight of hydrogen
as unity.

of gaseous sulphur and oxygen would be equal to the ratio between the weight of sulphur and half the weight of oxygen in sulphurous acid. In this way he found a value for the relative density of gaseous sulphur, and a value (31·73) for the molecular weight of sulphur gas referred to that of hydrogen as unity. Avogadro is careful to say that such methods as these give only "conjectural information" concerning the relative weights of molecules and the numbers of their constituent particles.

The hypothesis of Avogadro, that "the masses of molecules are in the same ratio as the densities of the gases to which they belong," strengthened the atomic theory by bringing within the cognizance thereof a class of facts concerning the combining volumes of gases which had seemed irreconcilable with it. This strengthening process was effected by modifying and amplifying the Daltonian theory; for the application of Avogadro's hypothesis to facts about the volumes of gases which react chemically made it necessary to think of two orders of minute particles, to distinguish the atom from the molecule. To accept the hypothesis was to have both a definition of the molecule and a simple and direct method of finding the relative weights of the molecules of all gaseous and gasifiable elements and compounds. Moreover, the hypothesis carried in itself the means of defining the atom, of determining the relative weights of atoms, and of discovering the numbers of atoms in the molecules of gasifiable substances.

By making more definite the meaning of the numbers which express the smallest relative masses of elements and compounds that take part in chemical reactions, and by suggesting a method whereby the most appropriate values for these numbers could be selected from the many possible values, the hypothesis of Avogadro advanced the solution of the two questions, What are chemically homogeneous substances? What happens when chemically homogeneous substances interact?

Finally, Avogadro's hypothesis put the generalization of Gay-Lussac on a firmer foundation, for it showed the close connexion between that generalization and the gravimetric compositions of compounds; and, while doing this, the work of Avogadro advanced the knowledge of the gaseous laws, and

prepared the way for a physical and dynamical theory of gases from which the Avogadrean hypothesis could itself be deduced.

If Avogadro's hypothesis was well-founded, the molecule of hydrogen was to be thought of as a group of two atoms; by referring the weights of molecules to the weight of a molecule of hydrogen taken as unity, not twice unity, and by omitting to state clearly the unit whereto atomic weights were to be referred, Avogadro slurred the distinction between the molecule and the atom. The hypothesis brought Gay-Lussac's generalization within the grasp of the atomic theory; but, as the facts to which that generalization was applicable were few, and not, apparently, supremely important, the greater part of chemistry seemed to lie outside the new conception introduced by Avogadro. That naturalist appeared to have made an excursion into a side-path, interesting in itself, but not then leading to any height of vantage.

The application of the conception of the molecule to the results of the study of composition could not be made until many attempts to arrange and systematize these facts without the help of that conception had failed. Despite its incompleteness, the Daltonian theory seemed to provide a strong and suitable scaffolding for proceeding with the building. The first question of chemistry, *What is a homogeneous substance?* had received a partial answer. Chemists attacked the second question, *What happens when elements and compounds interact?* It was only when the labours of many years had resulted in an immense confusion that they discovered in Avogadro's hypothesis, hidden under the "drums and tramplings" of half a century, the definitions of the element and the compound they had left unfinished, and the means of penetrating more deeply into the problems of chemical interactions.

Three years after the publication of Avogadro's memoir, that is, in 1814, a letter from Ampère to Berthollet appeared in *Annales de Chimie* (**90**, pp. 43–86), with the title, *Lettre de M. Ampère a M. le comte Berthollet sur la détermination des proportions dans lesquelles les corps se combinent, d'après le nombre et la disposition respective des molécules dont leurs particules intégrante sont composées.*

In that letter Ampère said that he was led by the work of Gay-Lussac to a

theory whereby the proportions of the constituents of many compounds could be determined. In preparing his memoir [1] he found that Avogadro had forestalled him. The hypothesis of Ampère is essentially the same as that of Avogadro, but a little more complicated, inasmuch as Ampère supposes that every molecule must be composed of at least four atoms. The greater part of Ampère's letter is concerned with an attempt to apply his conception of molecules to the facts of crystallography.

The attempts of the chemists of the first half of the nineteenth century to find values for the atomic weights of elements and compounds were based as much on the study of reactions as on that of composition. Before the results of the analyses of compounds could be expressed in consistent and comprehensive formulæ, in the language which was growing out of the laws of chemical combination, it was necessary, either to discover and use a method for finding the relative weights of the ultimate particles, both of elements and compounds, which was capable of direct application to particular cases, or to compare and contrast the reactions of the compounds analyzed, to class together those compounds which were chemically similar, to represent the compositions of their reacting particles by formulæ which seemed suitable, on the whole, and then to deduce values for the atomic weights of the elements whereof these compounds were composed. Until chemists realized the meaning of Avogadro's hypothesis, they were compelled to adopt the second of these methods, the laborious and unsatisfactory method of the comparison of reactions, for summarizing the results of the analyses of compounds.

Dalton's *New System* was published in 1808; the meaning of Avogadro's hypothesis began to be realized about the year 1860, after Cannizzaro had "tamed the word down to the ear" of the Congress of Chemists held that year at Carlsruhe. During these fifty years, multitudes of compounds were analyzed, many reactions were examined and classified, the combining weights of most of the elements were determined with considerable accuracy, and the multiples of these weights which were to be represented by the symbols of the elements, and would enable the compositions of compounds to be expressed by formulæ in

---

[1] Ampère seems not to have published the memoir he refers to; nothing is known of his work on the molecular theory beyond this letter to Berthollet.

keeping with their reactions, were selected, especially by Berzelius whose chemical instinct amounted to genius; and yet chemists failed to grasp the distinction between the two orders of small particles which Avogadro had indicated in 1811.

The deduction which Dalton made from Gay-Lussac's generalization, and rejected as untenable, that *equal volumes of homogeneous gases contain equal numbers of atoms,* was floating in the minds of chemists. Again and again attempts were made to seize and apply this statement, but the range of its applicability was so limited that little seemed to be gained by the attempts. Gradually, however, chemists were growing accustomed to the conception of an ultimate particle different from the Daltonian atom, and were getting weary of the confusion and contradictions which came into chemistry as the art of making formulæ became detached from the practice of studying facts. The need of a comprehensive theory, and the capricious outbreaks against the tyranny of facts which refused to arrange themselves in a clear mental picture of chemical occurrences, prepared the way for the use of the generalization of Avogadro as a means of classifying what was known and discovering much that was unknown.

As examples of the methods used in the first half of the nineteenth century for determining the relative weights of the ultimate, or reacting particles of elements and compounds, I shall consider very briefly some of the work, in this field, of Berzelius, Mitscherlich, Dulong and Petit, Dumas, Laurent, and Gerhardt.

In the last chapter I referred to the labours of Berzelius on the compositions of compounds.[1] Berzelius paid much attention to analyses of oxides, and compounds formed by the union of two or more oxides with one another. "Oxygen," Berzelius said, "is the measure in terms whereof the proportions between the constituents of all [inorganic] compounds can be determined." He laid great stress on a rule deduced from the results of analyses, that the quantity of

oxygen in a determinate weight of an electronegative oxide
(or, as we now say, an acidic oxide) is always a whole multiple
of the oxygen in that weight of an electropositive (or basic)
oxide wherewith the negative oxide combines to form a salt,
and that the number which expresses how many times the
weight of oxygen in a negative oxide is greater than the oxygen
in that weight of a positive oxide which combines with the nega-
tive oxide also generally expresses the number of atoms of
oxygen in the negative oxide. This generalized result of ex-
perience was extended to the mutual combinations of several
oxides, and helped Berzelius to choose the most suitable, from
the various possible formulæ for many series of salts. For
instance; Berzelius found that x grams of chromium combined
with y grams of oxygen to form an electropositive oxide, and
with $2y$ grams of oxygen to form a negative oxide. The most
suitable formulæ for the two oxides seemed to be CrO and
CrO_2, where Cr represents the weight of chromium which com-
bines with one atomic weight of oxygen. But Berzelius found
that the weight of oxygen in that quantity of the negative
oxide of chromium (chromic acid) which combined with a posi-
tive oxide to form a salt was three times the weight of the oxy-
gen in the positive oxide; hence he concluded that chromic acid
had the composition CrO_3, and the positive oxide of chromium
had the composition $CrO_{1\frac{1}{2}}$, or, preferably, Cr_2O_3. The first
pair of formulæ, CrO and CrO_2, gave the value 17·33, or 34·66,
or 216·66, for the atomic weight of chromium, according as
the atomic weight of oxygen was taken as 8, 16, or 100; the
second pair of formulæ, Cr_2O_3 and CrO_3, gave the value 26, or
52, or 325, for the atomic weight of chromium, the atomic
weight of oxygen being taken as 8, 16, or 100.

The formulæ of the two oxides of chromium could not be
regarded as settled until many compounds of each oxide had
been compared, both in composition and reactions, with several
other series of salts which resembled them chemically. And
when this had been done, and the formulæ Cr_2O_3 and CrO_3
adopted, some one might propose to double these formulæ,
and write Cr_4O_6 and Cr_2O_6. That proposal would be met by
saying, "the simpler formulæ, Cr_2O_3 and CrO_3, express the facts

as well as the more complex formulæ, why then change them?" Berzelius went farther than this, and declared that in considering a series of compounds of two elements, one compound must always be represented as containing a single atom of one of the elements. He said it was illogical to express the compositions of a series of oxides of an element, A, by the formulæ A_2O_2, A_2O_4, A_2O_6, etc.: the formulæ AO, AO_2, AO_3, etc., must be used; for, if the simplest oxide was A_2O_2, then the atoms of the element A could be divided mechanically.[1]

The rules which Berzelius deduced from his analyses and studies of reactions did not enable him to decide finally between the several possible values of the atomic weight of an element and the several possible formulæ of the compounds of the element. In 1813–1814 Berzelius said that the atomic weights of the elements are the weights of unit volumes of them in the state of gas, determined either directly or indirectly. Gaseous mercury was calculated by him to be about 25 times heavier than oxygen, on the assumption that oxide of mercury is analogous volumetrically to nitric oxide; and values were calculated for the relative densities of various other elements, which had not been gasified, by methods based on analogies between compounds of the elements of unknown vapour-densities and compounds of elements which had been gasified. Such methods were, of course, unsatisfactory. Starting from other assumptions, Gay-Lussac calculated the density of gaseous mercury to be about 12·5 referred to oxygen as unity.

For a time Berzelius preferred to speak of the weights of the combining volumes of the elements rather than to use the expression " atomic weights "; but as very few elements had been gasified, and the indirect methods of determining vapour-densities gave unsatisfactory results, Berzelius abandoned his hypothesis of volumes. At a later time he revived it in a restricted form, and applied the statement *equal volumes, equal number of atoms*, only to elements, and only to those elements which had not been liquefied or solidified. (See

---

[1] Dalton (*Thomson's Annals of Philosophy*, **3**, 174 [1814]) did not admit the justness of Berzelius' reasoning.

vol. v of 3d edition of his *Lehrbuch* [1835].)   But even in this
form the hypothesis was not generally accepted by chemists.
In his *Annals of Philosophy* for 1815 (**5**, 12), Thomson says
he could not find any advantage in the Berzelian hypothesis
of volumes.   "But," he adds, "Berzelius has deserved so well
of chemistry, that he may be indulged in any innocent whim
which produces no deterioration."   Berzelius repaid Thomson's
gibe with interest.   Speaking of Thomson's determinations of
atomic weights, Berzelius said (in his *Jahresberichte* for 1827),
"The greatest consideration which contemporaries can show
to the author is to treat his book as if it had never ap-
peared."

Berzelius, and those who came after him, made much use of
two methods for deciding between the possible values of the
relative weights of the ultimate particles of elements and
compounds, both of which are founded on certain physical
properties of homogeneous substances.   One of these methods
depends on the connexions between the compositions and the
crystalline forms of compounds, and the other on connexions
between the specific heats and the atomic weights of ele-
ments.

In the early years of last century, the opinion prevailed
that identity of crystalline form accompanied identity of chem-
ical composition, and each chemically homogeneous substance
crystallized in one form only.   Haüy's classification of minerals
was founded on this supposition; and that classification, Ber-
zelius tells us in his *Jahresberichte* for 1822 (p. 67), advanced
year by year triumphantly (*auf eine sehr triumphirende Weise*).
But in 1819 Mitscherlich announced that the crystalline forms
of certain phosphates were the same as those of certain arsen-
ates, although one series of salts contained phosphorus and the
other contained arsenic.   He extended his observations to other
salts, and found many instances of identity of crystalline form
accompanying differences of chemical composition.[1]

---

[1] Eilhard Mitscherlich (born 1794 in Oldenburg) noticed that the crystalline
forms of certain arsenates and phosphates were the same.   He asked G. Rose
to instruct him in crystallography, and he taught Rose the methods of chemical
analysis.   In 1819 he went to Stockholm and worked in Berzelius' laboratory.

Two years later, Mitscherlich published a lengthy memoir wherein he gave a full account of his researches into the following problems: Have the combinations of different elements with the same number of atoms of another element, or other elements, the same crystalline form? Is identity of crystalline form determined only by the number of atoms, and is it independent of the chemical nature of the elements?

Mitscherlich analyzed eight pairs of arsenates and phosphates—simple, double, and acid salts of the alkali metals, and salts of lead—and gave elaborate descriptions of their properties, especially of their crystalline forms.[1] He summarized his results as follows.[2]

"*The same substance, formed from the same quantities of the same constituents, may exhibit two different crystalline forms*, in accordance with conditions at present unknown. This phenomenon may be understood by the help of the atomic theory: different forms will be assumed when the relative positions of the atoms are different; but, on this supposition, the number of particular forms of a substance will be very limited. No phenomenon stands alone in physical science; the laws we have discovered may be extended to the whole subject of the formation of crystals. What has been observed in a salt must hold good for oxides also; this is in agreement with the proposition laid down in an earlier part of this memoir, that various chemical compounds of similar composition may be arranged in classes of *isomorphous substances*,

---

His first memoir was published in the Berlin Academy's Proceedings for 1818–1819; in a somewhat extended form it appeared in *Annal. Chim. Phys.* for 1820, with the title, *Sur la Relation qui existe entre la forme cristalline et les proportions chimiques. Premier Mémoire sur l'identité de la forme cristalline chez plusieurs substances différentes, et sur le rapport de cette forme avec le nombre des atomes élémentaires dans les cristaux.* In 1821 Mitscherlich published a long memoir on the arsenates and phosphates in the Swedish Academy's Proceedings. A translation, made by himself, appeared the same year in *Annal. Chim. Phys.* [2], **19**, 350: *Sur la Relation qui existe entre la forme cristalline et les proportions chimiques. IIme Mémoire sur les Arséniates et les Phosphates.* A translation of the first memoir was published in *Quart. J. of Science* for 1822–23, **14**, 198, 415. All Mitscherlich's memoirs were published together in 1896, with the title, *Gesammelten Schriften von Eilhard Mitscherlich* [S. Mittler & Sohn, Berlin]. No. 94 of Ostwald's *Klassiker der exakten Wissenschaften* is a reprint (from the *Gesammelten Schriften*) of Mitscherlich's second and most important memoir.

[1] The first part of Mitscherlich's memoir, dealing only with his methods of determining and expressing the forms of crystals, does not appear in *Annal. Chim. Phys.*, nor in Ostwald's edition of his memoir. Mitscherlich used the methods of spherical trigonometry in his calculations, whereas his predecessor (to whose works he gives references) used only the procedure of plane trigonometry.

[2] In the text I give a fairly free translation of the passages italicized on pp. 52, 53 of Ostwald's edition, after comparing them with the corresponding passages in *Annal. Chim. Phys.* [2], **19**, 415–417.

that is, substances which have the same crystalline form.[1]   The reason why
a group of isomorphous substances always maintains the same form, which
is different from the forms of other groups, is . . . to be found in the different
relative positions of the atoms. I have illustrated this proposition by various
examples.   I have shown that lime, magnesia, oxide of manganese, ferrous
oxide, oxide of copper, of zinc, of nickel, and of cobalt belong to the same
group of isomorphous compounds; in this group, one atom of metal is com-
bined with two atoms of oxygen. . . .   Chemical reasons oblige us to regard
the oxides of lead, of strontium, and of barium as formed by the union of one
atom of metal with two atoms of oxygen; these oxides also form an iso-
morphous group, but the crystalline form of this group is different from that
of the first group of oxides. . . .   The forms of the members of these two
groups must be conditioned by differences in the positions of the two atoms
of oxygen relatively to the atom of metal."

Mitscherlich then quotes descriptions of the various crystalline
forms of calcium carbonate, and compares the crystals of this
compound with those of lead carbonate and those of strontium
carbonate.   He concludes by enunciating the general laws of
the connexion between crystalline form and chemical compo-
sition: "*Equal numbers of atoms, combined in the same manner,
produce the same crystalline forms; identity of crystalline form is
independent of the chemical nature of the atoms, and is determined
only by their number and relative positions.*"   I will give two ex-
amples of the use of the law of isomorphism in questions con-
cerning the relative weights of the ultimate particles of elements
and compounds.

In his *Leçons sur la Philosophie chimique*, Dumas said that
the formulæ Cu_2S and AgS, given at that time (1836) to the
sulphides of copper and silver, could not both be correct, because
the compounds are isomorphous, and identity of crystalline
form accompanies equality of numbers of atoms.   Dumas gave
reasons for accepting the formula Cu_2S for sulphide of copper,
and proposed the formula Ag_2S for sulphide of silver.   If the
atomic weight of sulphur was not altered, the change in the
formula of the silver compound from AgS to Ag_2S necessitated
the adoption of a value for the atomic weight of silver half as
great as that which had been used before.

---

[1] Near the beginning of this second memoir (p. 4, Ostwald's Edition), Mit-
scherlich said: " Certain elements combine with the same number of atoms of
another element, or of other elements, to produce compounds of the same crystal-
line form.   In this regard the elements may be divided into groups. . . . I have
called the elements which belong to the same group, *isomorphous elements*."

The isomorphism of four compounds, found as minerals, named *apatite, pyromorphite, mimetesite*, and *vanadinite*, was established in 1856. The formulæ given to these compounds when Roscoe began his researches on vanadium (in the sixties of last century) were, $3(3CaO \cdot P_2O_5)CaCl_2$; $3(3PbO \cdot P_2O_5)PbCl_2$; $3(3PbO \cdot As_2O_5)PbCl_2$; and $3(3PbO \cdot V_2O_3)PbCl_2$, respectively. Assuming the correctness of the first, second, and third formula, Roscoe [1] argued that the formula given to *vanadinite* was wrong and ought to be changed to $3(3PbO \cdot V_2O_5)PbCl_2$. Berzelius had given the value 68·5 to the atomic weight of vanadium, as the result of reducing the highest oxide of the metal in a stream of hydrogen, and weighing the metal-like residue which he assumed to be vanadium; the formula V_2O_3, therefore, asserted that vanadium and oxygen were combined, in a certain oxide, in the ratio 45·66:16. Roscoe's proposal seemed equivalent to the assertion that the ratio 27·4:16 was that in which vanadium and oxygen were combined in the oxide in question.[2] The result of a series of experiments, made with great care by Roscoe, was to establish the ratio 20·48:16 as that of the weights of vanadium and oxygen in the oxide, and to show that the atomic weight of vanadium must be 20·48, or a number simply related thereto. After much labour, Roscoe proved that the substance supposed by Berzelius to be vanadium was a compound of that metal with oxygen, wherein the two elements were combined in the ratio 51·2:16; as no oxide of vanadium could be obtained containing less oxygen than this, Roscoe gave the value 51·2 to the atomic weight of vanadium, and the formula V_2O_5 (where V=51·2) to the oxide represented by Berzelius [3] as V_2O_3 (where V=68·5).

Determinations of the crystalline forms of similar compounds of vanadium, of arsenic, and of phosphorus led not only to an alteration of the atomic weight of vanadium and the reconstruction of the formulæ of all the compounds of that metal, but also to the demonstration that a substance said to be a

---

[1] *Phil. Trans.* for 1868, p. 1.
[2] $V_2O_3 = 137:48 = 45·66:16$. $V_2O_5 = 137:80 = 27·4:16$,   taking V=68·5 and O=16.
[3] V_2O_5 might be written $(VO)_2O_3$.   (VO)=51·2+16=67·2.

metal by the greatest of all analytical chemists was a compound of a metal with oxygen.

The progress of the investigation of the connexions between crystalline form and composition has shown that Mitscherlich's *law of isomorphism* is not a sufficiently full and precise description of facts to serve as the foundation of a method for selecting the most suitable value for the atomic weight of an element, or the molecular weight of a compound, from the various possible values, and has indicated that the chief service which this *law* can render, in problems dealing with atomic and molecular weights, is to suggest lines of research which may be followed up by other methods.

The same chemically homogeneous substance sometimes crystallizes in different forms. In Mitscherlich's statement, "Equal numbers of atoms, combined in the same manner, produce the same crystalline forms," the word *atoms* must be taken to include atomic groups; this at once opens a wide field for inquiry. The phrase "combined in the same manner" is vague, but no more precise form of words has been found which can make the statement more directly serviceable. The outcome of the more recent work on the connexions between crystalline form and composition is stated thus in the article "Isomorphism" in *Watts' Dictionary of Chemistry* (new ed.), vol. iii, p. 89: "At present, crystal-form cannot be deduced from a knowledge of chemical constitution and properties alone; if, however, we find that in a given case certain atoms arranged in a certain definite way are accompanied by a certain definite form, we may argue that similar atoms similarly arranged will be accompanied by a similar form." [1]

In 1819 was published a memoir entitled *Recherches sur quelques points importants de la théorie de la Chaleur. Par MM. Petit et Dulong.* [2] The authors gave the results of their measurements of the specific heats of thirteen solid elements. The

---

[1] The article referred to in the text may be read with advantage by the student. Reference to other general articles on Isomorphism will be found there. The subject of the connexions between crystalline form and chemical composition is admirably treated from the historical position in Chapter XV of Miss Freund's *A Study of Chemical Composition* [1904].

[2] *Annal. Chim. Phys.* [2], **10**, 395.

specific heats were determined, by the method of cooling, for an interval of temperature from 5° to 10° above the temperature of the surrounding air, precautions being taken to insure that the temperature of the surrounding air was the same in all the experiments and was constant during each experiment.

The following table contains the results of Petit and Dulong.

	Specific heats.	Relative weights of the atoms.	Products of the weight of each atom into the corresponding capacity.
Bismuth.	·0288	212·8	6·128
Lead.	·0293	207·2	6·070
Gold.	·0298	198·8	5·926
Platinum.	·0314	178·5	5·984
Tin.	·0514	117·6	6·046
Silver.	·0557	108	6·030
Zinc.	·0927	64·5	5·977
Tellurium.	·0912	64·5	5·880
Copper.	·0949	63·3	6·008
Nickel.	·1035	60	5·904
Iron.	·1100	54·3	5·969
Cobalt.	·1498	39·4	5·896
Sulphur	·1880	32·2	6·048

Those atomic weights were selected which the authors considered to be in accord with the most firmly established chemical analogies.[1]

The products of specific heats into atomic weights are so nearly equal, Petit and Dulong said, that one is forced to regard the differences as due to errors of experiment; and the number and diversity of the elements examined make it impossible that the relation between specific heat and atomic weight shown in the table should be fortuitous.[2]

From these results Petit and Dulong deduced the law, *Les*

[1] In the original, atomic weights are referred to that of oxygen as unity. I have multiplied the values given for atomic weights, and for the products of specific heat into atomic weight, by sixteen.

[2] Most of the values given in the table for specific heats agree approximately with those obtained more recently: the specific heats assigned to tellurium and cobalt are, however, very erroneous; that given to tellurium is nearly twice the true value, and the specific heat of cobalt is less than the value given in the table in the ratio approximately of 1·4:1. The atomic weights in the table do not differ greatly from those used to-day, except in the cases of platinum (atomic weight about 194), tellurium (atomic weight about 126), and cobalt (atomic weight about 59). The errors in the atomic weights given to tellurium and cobalt are compensated by the errors in the specific heats assigned to these elements.

atomes de tous les corps simples ont exactement la même capacité pour la chaleur.

The authors said that this law must help to control the results of chemical analyses, and that it affords a very exact method for arriving at a knowledge of the proportions of the elements in certain compounds. They remarked that the values found by other experimenters [1] for the specific heats of oxygen and nitrogen agreed with their law, within the limits of experimental errors, and that, although the specific heat of hydrogen was somewhat too small, nevertheless it might be regarded as confirming the law when the difficulties in the way of an accurate determination were considered.

The application of the *law of atomic heat* was very simple: the minimum value for the atomic weight of an element was obtained from analyses of compounds of the element, and that multiple of this minimum value was chosen which, multiplied into the specific heat of the element, gave a number approximately equal to 6.

The results of the more searching examinations into the connexions between the specific heats and the atomic weights of the elements, which have been made since the publication of Petit and Dulong's memoir in 1819, have made it necessary to modify the law enunciated by these naturalists, and to limit its application to the solid elements.

As an example of the kind of work which has been done, let us consider very briefly the specific heat of beryllium. In 1880 Nilson and Pettersson (*Berichte*, **13**, 1456) determined the specific heat of this element for various intervals of temperature, working with a specimen of the metal which contained about 5 *per cent.* of oxides of beryllium and iron, and proved the specific heat to be about 27 *per cent.* greater between 0° and 300° than between 0° and 50°. In the same year, Lothar Meyer (*l. c.*, **13**, 1780) showed that the data obtained by Nilson and Pettersson made it very probable that the specific heat of beryllium increases rapidly as temperature increases, that the rate of increase is less at high than at low temperatures, and

---

[1] Especially Bérard and Delaroche, *Annal. Chim. Phys.*, **85**, 72 [1813].

that the specific heat attains a constant value at about 300°. A few years later, Humpidge (*Proc. R. S.*, **39**, 1) directly determined the specific heat of beryllium at different temperatures, and found that the value approximates to a constant, about ·62, at somewhere between 300° and 400°.

The following statement would have been accepted about the close of the nineteenth century as a fairly accurate description of what was then known concerning the connexion between the specific heats and the atomic weights of the elements. If the temperature whereat the thermal capacity of each element is stated is such that the value of this ratio has become constant, then the atoms of all solid elements have approximately the same capacity for heat.   The value of the product of specific heat multiplied by atomic weight approximates to 6·2.

About 1897, Tilden began an investigation of the specific heats of elements and of compounds throughout long ranges of temperature. In 1905 he gave a *résumé* of his results and general conclusions in the *Journal of the Chemical Society*.[1]   I quote some of his conclusions.

"The influence of temperature on the specific heats of many elements and compounds is much greater than was formerly supposed. There appears to be no one condition or set of conditions under which the law of Dulong and Petit is true of all the elements.   The nearest approach to a constant available for practical purposes is found by taking the mean specific heats of metals between the freezing and boiling points of water, recognizing glucinum [beryllium], boron, carbon, and silicon as exceptions, together with hydrogen, oxygen, nitrogen, and perhaps chlorine in the solid form."

Petit and Dulong gave no data concerning the specific heats of compounds; they said that there is always a simple relation beween the capacities for heat of compound atoms and the capacities for heat of elementary atoms. In 1831, F. Neumann (*Pogg. Annal.*, **23**, 1) declared that equivalent weights of compounds of similar composition have equal capacities for heat: this statement received general confirmation from the results of a long series of determinations of the specific heats of elements and compounds made between 1836 and 1861 by

---

[1] *C. S. Journal*, **87**, 551 [1905].   References to Tilden's earlier memoirs are given in this communication.

Regnault.[1] In 1858 Cannizzaro founded a method for determining the specific heats of atoms in combination on the statement, made by Garnier in 1852,[2] that the capacities for heat of atoms are not much changed by combining with one another. Cannizzaro's generalization may be expressed thus: if the products obtained by multiplying the molecular weights into the specific heats of solid compounds are divided by the number of atoms in the molecule of each compound, the quotients have approximately the same value, namely, 6·2.[3]

A great deal of work has been done on the connexions between the specific heats and the molecular weights of compounds since 1858, notably by Kopp;[4] the general result has been to show that the generalization of Cannizzaro and Garnier holds good in many cases, but not in all. Tilden's results (C. S. Journal, 87, 551 [1905]) tend to show that the specific heats of the atoms in many solid compounds are not affected by the chemical combination of these atoms; in other words, that the molecular heats of many compounds are the sum of the atomic heats of their elements.

It is evident that a complete theory of specific heat, even if it be confined to gases, must take account of the nature and the arrangement, as well as the number of the atoms which form compound molecules. The specific heat of a compound molecule is probably equal to the sum of the specific heats of the constituent atoms only when the distance between any pair of atoms is approximately equal to the distance between any other pair; but there can be little doubt that, in many compound molecules, certain atoms are more closely associated with one another than any of them are associated with the other atoms.[5]

Although, in the earlier decades of the nineteenth century, no simple method of determining the relative weights of the

[1] Annal. Chim. Phys. [2], 63, 5; [3], 1, 129; 9, 322; 26, 261, 268; 38, 129; 46, 257; 63, 5.
[2] Compt. rendus, 35, 278; 37, 150.
[3] Compare p. 122.
[4] See, especially, Annal. Chem. Pharm., Supplbd., 3, 1, 289 [1864–5]; and Berichte, 19, 811 [1886].
[5] A much fuller historical treatment than I have given of the connexions between atomic weights and specific heats will be found in Chapter XIV of Miss Freund's A Study of Chemical Composition [1904].

ultimate particles of elements and compounds was in general use, although the distinction between the atom and the molecule was not realized, nevertheless chemists rested their modes of expressing the compositions of compounds, and the values they gave to the atomic weights of elements, on an hypothesis which made a large assumption regarding the structure of the ultimate particles of compounds; for it assumed these particles to be composed of two portions, one positively and the other negatively electrified, and regarded the stability of the particles to be due to the neutralization of the positive electricity of one portion by the negative electricity of the other.

The dualistic hypothesis, founded by Lavoisier and greatly developed by Berzelius, will be considered in a later chapter (Chapter IX): at present I wish to give only a brief sketch of certain aspects of it sufficient to help the student to understand the bearing of this part of the work of Berzelius on the later developments of the molecular and atomic theory.

Berzelius pictured to himself several stages in the formation of an atom of a complex compound: the first stage was the union of an atom of an electrically positive element with an atom of an electrically negative element to form a compound atom of the first order; the second stage was the union of this compound atom with another of like complexity, but the electrical opposite of the first; if the combination was carried further, the third stage consisted in the union of the compound atom of the second order with another oppositely electrified atom of the same order. The decomposition of a complex atom was thought of by Berzelius as, primarily, the separation of the atom into two parts of opposite electric signs, each of which could be separated into two electrically opposed portions, and so on, until finally a pair of elementary atoms was obtained, one positively and the other negatively electrified.

This conception of the structure of compound atoms led Berzelius to suppose that the formation of one compound from another chemically like it consisted in the replacement of an atom, or a group of atoms, in the ultimate particle of the first compound, by an atom, or a group, of the same electrical sign as that which it replaced. Berzelius would not admit that a

positive atom, or atomic group, could be replaced by a nega-
tive atom, or atomic group, and the product be chemically like
the parent compound. The chemical type was maintained, he
asserted, only when the electric charges on the replacing atoms
or atomic groups were of the same sign as the electric charges
on the atoms or groups which they replaced.

This hypothesis, which was, of course, an outcome of the
examinations of certain reactions, regarded the ultimate par-
ticle of every compound as a dualistic structure, and for many
years the results of the analyses of compounds were expressed
in formulæ based on this conception.

When the dualistic hypothesis was in vogue, the primary
object of most chemists was to represent every compound by a
formula constituted of two atoms, or groups of atoms. Investi-
gation of reactions was pursued with but little zeal; for the
only mode of representing the results was dualistic formulæ,
a language almost incapable of expressing the relations between
compounds. If observed reactions did not agree with deductions
from the hypothesis, so much the worse for the reactions. When
a simple formula did not serve for the presentation of a com-
pound as a dualistic structure, it was easy to double, treble,
or quadruple the formula, until an expression was obtained
which could be cut into two parts, one of which might be as-
serted to be the electric counterpart of the other. Formulæ
became cumbrous and repellant; they were mere "paper bul-
lets of the brain"; at times it was almost true that as many
chemists so many formulæ for the same substance. Many
reactions of compounds, whose compositions were expressed by
formulæ containing four, six, eight, or more atoms of this or
that element, could be expressed equally well by simpler for-
mulæ, sometimes even by formulæ containing a single atom of
the element in question, provided the value commonly given
to the atomic weight of the element was doubled. Some
chemists preferred the simpler formulæ, and used atomic weights
twice as great as those used by others. Hence arose a mighty
confusion; a confusion but little alleviated by the hypothesis
of Berzelius that double atoms of certain elements always take
part in chemical reactions, and the representation of these

double atoms by the ordinary symbols of the elements with a bar drawn across them.

It was only the overpowering genius of Berzelius, and the quantity and accuracy of his work, which secured the dominancy of the dualistic system. That system was overthrown by the labours of many chemists, notably by Laurent and Gerhardt. Before considering some of the work of these men, I ask the student's attention to what was done by Dumas towards classifying and simplifying the expressions of composition and reactions, and more particularly to the uses he made of the generalization of Gay-Lussac concerning the combining volumes of elements and compounds.

As early as 1826, Dumas accepted the statement that equal volumes of gases contain equal numbers of particles. In a memoir published that year [1] he refers to Ampère's hypothesis,[2] that the particles of simple gases divide into portions in chemical reactions; recognizes the great importance of determining the relative densities of elements and compounds in the state of gas; describes a method for measuring vapour-densities which has been much used since that time; and gives the results of his determinations of the relative densities of gaseous iodine, mercury, phosphorus trichloride, arseniuretted hydrogen, arsenic trichloride, silicon tetrachloride, hydrofluosilicic acid, boron trichloride, fluoboric acid, stannic chloride, and titanic chloride. Six years later, Dumas determined the vapour-densities of phosphorus, sulphur, and several other substances.[3]

In 1836 Dumas delivered a course of lectures on chemical philosophy.[4] In the seventh lecture, which treats of the volumetric combinations of gases, and subjects allied thereto, Dumas applied the generalization, *equal volumes equal numbers of atoms*, to the volumetric combinations of hydrogen and chlorine to form hydrochloric acid, and nitrogen and oxygen to form nitric oxide, and showed that, if the generalization is accepted, the atoms of the four elements concerned must be cut into at least two

---

[1] *Annal. Chim. Phys.* [2], **33**, 337.
[2] Ampère was forestalled by Avogadro (see pp. 111, 112).
[3] *Annal. Chim. Phys.* [2], **49**, 210; **50**, 170 [1832].
[4] *Leçons sur la Philosophie chimique professées au Collège de France.* The quotations in the text are from the second edition, published in 1878.

parts in these reactions.   To the objection that it is absurd to
define the atom as an indivisible particle, and then to assert that
these particles are cut into two in the formation of certain com-
pounds, Dumas replied, "*La Chimie coupait les atomes que la
Physique ne pouvait pas couper.   Voila tout.*"   But some chem-
ists would not recognize the distinction assumed in this sentence
between physical atoms and chemical atoms, and would limit
the application of the generalization, *equal volumes equal num-
bers of atoms*, to gaseous elements.   Even if you accept this
limitation, Dumas said, you are met by difficulties.   The rela-
tive densities of oxygen, nitrogen, chlorine, bromine, and gaseous
iodine give atomic weights for these elements which are accepted
by every one, because they are in agreement not only with the
generalization but also with all the requirements of chemistry.
Now phosphoretted hydrogen and ammonia are very similar
chemically: ammonia is formed by the union of a volume of
nitrogen with three volumes of hydrogen; therefore phospho-
retted hydrogen is to be regarded as formed by the union of a
volume of phosphorus-gas with three volumes of hydrogen.   In
other words, the replacement of the nitrogen in ammonia by an
equal volume of phosphorus-gas will produce phosphoretted
hydrogen; from this, and from determinations of the weight of
phosphorus which replaces the nitrogen combined with three
parts by weight of hydrogen in ammonia, it follows that the
densities of hydrogen and phosphorus-gas are in the ratio
$1:31\cdot4$, but experiment shows the ratio of these densities to be
$1:62\cdot8$.   Similar data and reasoning lead to the conclusion that
the ratio of the densities of hydrogen and arsenic-gas is $1:75\cdot3$,
but experiment gives the ratio $1:150\cdot6$.   The conclusion drawn
by Dumas was that some of the most beautiful analogies in
chemistry must be abandoned, or that equal volumes of gaseous
phosphorus, arsenic, and nitrogen do not contain equal numbers
of atoms.[1]

The gaseous particles of phosphorus and of arsenic, Dumas
said, seem to contain twice as many chemical atoms as the par-

---

[1] Dumas referred his vapour-densities to that of oxygen taken as 100; I have
reduced them to the standard of hydrogen as unity.

ticles of nitrogen; in these cases chemical action accomplishes
a more complete division of the particles than is effected by
heat.   On the other hand, heat seems to divide the gaseous par-
ticles of mercury more than chemical action; for, from the an-
alogy between compounds of mercury, lead, and zinc, it is neces-
sary to suppose that oxide of mercury is formed by the union of
equal volumes of mercury-gas and oxygen, and from the fact
that 202·6 parts by weight of mercury combine with 16 of
oxygen, one must take the density of mercury gas as 202·6,
referred to hydrogen as unity; but experimental determinations
show that the densities of mercury and hydrogen are in the
ratio 101·3 : 1.

If equal volumes of gases contain sometimes equal and
sometimes unequal numbers of atoms, it seemed to Dumas that
the study of the relative densities of gases could not be a trust-
worthy help towards determining atomic weights.   But it may
be said that equal volumes of gases contain equal numbers of
molecular or atomic groups.   If one makes this admission, Dumas
said, "*On contentera tout le monde; mais on ne donnera rien
d'utile à personne jusqu'à present.   Ce ne sera après tout qu'une
hypothèse, et sur ce sujet on n'en a déjà que trop fait.   Resumons
les faits.*"

Dumas concluded that the knowledge chemists had of gase-
ous combinations at that time was insufficient for the estab-
lishment of laws, and that it was necessary to gain more ac-
curate and wider knowledge by determining the relative densi-
ties of many gases both elementary and compound.   Dumas
thought that the equivalent weights of elements could not then
(1836) be fixed with certainty; analogy was the only method.
Atomic weights could not be determined from the considerations
used in trying to fix equivalent weights: the relative densities of
gases did not give atomic weights, nor could measurements of
the equivalent weights of acids, bases, or salts make chemists
acquainted with the atomic weights of the elements.   "Were it
not for isomorphism," Dumas said, "the atomic theory would
be a purely conjectural science."

Dumas was evidently feeling his way towards the differen-
tiation of the atom and the molecule, but he was unable at that

time to realize these two conceptions with sufficient vividness to make them directly applicable to the facts.[1]

He began with the atom as an indivisible particle; he was soon obliged to see that indivisible particle undergo division; he called in the aid of the physical atom, a collocation of chemical atoms, but he had not learned the proper use of the instrument; the connexion between the chemical atom and the group of chemical atoms which acted as a physical whole seemed arbitrary and capricious; that which could not be cut was cut, that which was divisible remained undivided. Dumas would fain have abolished the atom and returned to experience, forgetting, I suppose, that the atomic theory is merely a mode of expressing the results of experience and suggesting lines of experimental inquiry. "*Si j'en étais le maître,*" he exclaims, "*j'effacerais le mot atome de la science, persuadé qu'il va plus loin que l'expérience: et jamais en Chimie nous ne devons aller plus loin que l'expérience.*"

In 1850, Brodie[2] endeavoured to show that the reactions of elements and compounds are essentially similar, that the reacting weights of both classes of homogeneous substances are groups of minute particles.

In 1851 Williamson[3] thought that the reactions of certain elements were most completely described by assuming differences between the properties of the atoms and the molecules of these elements. In the same year he published his researches on the ethers,[4] wherein he deduced the molecular weights of these compounds from the study of their reactions, and prepared the way for the general application of the chemical method of determining molecular weights.

---

[1] On p. 306 of *Leçons* (2d ed.) Dumas says: " La matière est formée d'atomes. Les chaleurs spécifiques nous enseignent les poids relatifs des atomes des diverses sortes. La Chimie opére sur des groupes d'atomes de matèire. Ce sont ces groupes qui, en s'unissant dans différents rapports, produisent les combinaisons en suivant la loi des proportions multiples; ce sont eux dont le déplacement mutuel donne lieu de remarquer la règle des équivalents dans les réactions. Enfin la conversion en gaz ou en vapeur crée encore d'autres groupes moléculaires, dont dépendent les lois observées par M. Gay-Lussac."

On p. 315 Dumas says: " Ma conviction, c'est que les équivalents des chimistes, ceux de Wenzel, de Mitscherlich, ce que nous appelons *atomes*, ne sont autre chose que des groups moléculaires."

[2] *C. S. Journal*, **4**, 194; also *Phil. Trans.* for 1850, 759.

[3] *C. S. Journal*, **4**, 355.

[4] *Ibid.*, **106**, 229.

An English translation of Laurent's *Méthode de Chimie*[1] appeared in 1855; the fourth volume of Gerhardt's *Traité de Chimie Organique*[2] was published in 1856. These two works greatly helped the advance of chemistry by introducing order, consistency, and accuracy into the study of chemical reactions and the expressions of them in formulæ.

The dualistic system rested on a certain conception of the relations to one another of the parts of compound molecules. Both Laurent and Gerhardt gave many examples of the confusion and contradictions which had arisen from using this conception,[3] and both insisted that the times were not ripe for the representation of the structure of the ultimate particles of substances, and that the only way of bringing order and lucidity into chemistry was the comparative study of chemical reactions, and the presentation of these reactions and their mutual relations in a clear and intelligible language. The best formula for a compound, they said, was that which expressed the reactions of it in such a manner that the chemical similarities between the compound and other compounds were made evident. To form a clear, suggestive, and descriptive language, it was necessary to adopt a working hypothesis and to use certain conventions. Laurent and Gerhardt agreed that the hypothesis of molecules and atoms worked better than any other. If this hypothesis was to be directly helpful, the expression *molecular weight* had to be defined; then it would become possible to define *atomic weight*. Gerhardt said that the molecular weight of an element or compound is the smallest quantity of it which takes part in chemical reactions, and asserted that the most consistent and illuminating results are obtained by taking

[1] *Chemical Method, notation, classification, and nomenclature,* by Auguste Laurent; translated by William Odling [Harrison & Sons, London, 1855]. The French original was published in 1854, after the death of Laurent.

[2] *Traité de Chimie Organique,* par M. Charles Gerhardt (Tome quatrième) [Firmin Didot Frères, Fils et Cie., Paris, 1856].

[3] More than one value was used for the atomic weight of an element; the same compound was represented by many formulæ; and the same formula was given to more than one compound. To some chemists, the formula H_2O_2 meant water, and to others it represented hydrogen peroxide; $C_4H_4O_4$ was taken by some to be the formula of acetic acid, and by others to be the formula of fumaric or of maleic acid. The composition of water was expressed sometimes by H_2O, and sometimes by H_2O_2. The symbols C, O, and S might mean one, or two atoms of carbon, oxygen, and sulphur, respectively.

the molecular weight to be, in almost every case, the weight of that quantity of the element or compound which occupies, in the gaseous state, twice the volume occupied by a unit weight of hydrogen.   Laurent adopted this convention except in the cases in which it led to formulæ of compounds containing fractional numbers of atoms;[1] in these cases, he said, it was better to take, as the molecular weights of compounds, those weights of them which occupied, in the gaseous state, four times the volume occupied by the unit weight of hydrogen.   Atomic weights then became, according to Laurent, the weights of the smallest quantities of the elements which can exist in combination.

Gerhardt used the same values as Berzelius for the atomic weights of the elements, except in the cases of metals, where he divided the Berzelian values by two; he also halved very many of the molecular weights assigned to compounds by Berzelius. In Gerhardt's system, the molecular weights of hydrogen, chlorine, water, nitric acid, and sulphuric acid were severally expressed by the formulæ HH, ClCl, H_2O, HNO_3, and H_2SO_4.

Most of the formulæ used by Gerhardt and by Laurent were the same as those we use to-day: these men expressed their conception of the molecule and the atom in terms found in almost every modern text-book; yet something was wanting which neither of these great naturalists supplied.   A more complete realization of the molecule and the atom was required, a more vivid mental picture of the minute structure of homogeneous substances was needed, before the reactions, the chemical similarities and dissimilarities, of these substances could be simply and directly connected with the compositions of their ultimate particles.   The time of this clearer vision was near. Laurent's book was published in 1854, Gerhardt's in 1856; Lothar Meyer tells us the scales fell from his eyes in 1860 and he saw.

A congress of chemists was called at Carlsruhe in 1860 to consider whether any way could be discovered out of the confusion and bewilderment of formulæ, hypotheses, and con-

---

[1] We shall see that, in these cases, the gases obtained by heating the compounds are mixtures, and the apparent exceptions to the rule are not real.

ventions. Lothar Meyer has told (in the notes to Ostwald's edition of Cannizzaro's pamphlet) that at the close of the conference he received a pamphlet by Cannizzaro, which had appeared a few years before, but had met with scanty notice. When he got home, Meyer read the pamphlet, and, as he says, "*Es fiel mir wie Schuppen von den Augen, die Zweifel schwanden, und das Gefühl ruhigster Sicherheit trat an ihre Stelle.*"

Cannizzaro's pamphlet [1] gave an account of the lectures he was accustomed to deliver, towards the end of the fifties, on the applications of the molecular and atomic theory to chemical reactions. In 1872 Cannizzaro delivered the Faraday Lecture before the Chemical Society.[2] In that lecture he gave an account, on the same lines as in his earlier publication, of his methods of teaching theoretical chemistry.

Cannizzaro made clear, in 1858, how the study of chemical reactions alone had failed to lead to a consistent representation of these reactions in terms of the atomic theory, which, nevertheless, was the only machinery for expressing, comparing, and classifying the facts of chemistry that had commended itself to chemists. He declared that the addition to the atomic theory made by Avogadro and Ampère must be adopted unreservedly, as a working hypothesis, if all the parts of chemistry were to be brought into an harmonious whole; and he asserted that the applications of Avogadro's hypothesis led to conclusions in keeping with all the chemical and physical laws then known.

Cannizzaro then showed how Avogadro's generalization enabled determinations to be made of the relative weights of molecules, without previous knowledge of the compositions of these molecules or of their reactions; it was only necessary to find the relative densities of the substances, elements or compounds, in the gaseous state. In his selection of the unit

[1] *Sunto di un corso di filosofia chimica fatto nella Reale Università di Genova dal Professore S. Cannizzaro.* Published in *Nuovo Cimento,* vol. vii [1858]. Translations into German of this pamphlet, and of two other brief papers on vapour-densities by Cannizzaro, form No. 30 of Ostwald's *Klassiker der exakten Wissenschaften.* [W. Engelmann, Leipzig, 1891.]

[2] *Considerations on some Points of the Theoretic Teaching of Chemistry. C. S. Journal,* [2] **10,** 941 [1872].

to which the vapour-densities of substances were to be referred, Cannizzaro differed from Avogadro: the latter referred molecular weights to that of hydrogen as unity; Cannizzaro said:

"Instead of taking for your unit the weight of an entire molecule of hydrogen, take rather the half of this weight, that is to say, the quantity of hydrogen contained in the molecule of hydrochloric acid." [1]

This change of unit was a little thing, yet it was fraught with great results; it brought home to chemists the principle they had been seeking for half a century, it put into their hands the instrument they required and had overlooked.

Cannizzaro gave the following table of vapour-densities and molecular weights.[2]

Name of substance.	Densities or weights of a gaseous volume, referred to the weight of a volume of hydrogen = 1; or molecular weights referred to the weight of a molecule of hydrogen as unity.	Densities referred to that of hydrogen taken as 2; or molecular weights referred to the weight of a semi-molecule of hydrogen as unity.
Hydrogen.................	1	2
Ordinary oxygen...........	16	32
Electrified oxygen..........	64	128
Sulphur under 1000°........	96	192
" over 1000°..........	32	64
Chlorine..................	35·5	71
Bromine.	80	160
Arsenic.	150	300
Mercury...................	100	200
Water.....................	9	18
Hydrochloric acid...........	182·5	36·5
Acetic acid.................	30	60

This table shows that Cannizzaro at once accepted a startling conclusion arising from the application of Avogadro's hypothesis, namely, that the same element sometimes has more than one molecular weight.

Cannizzaro then proceeded to examine the compositions of molecules the relative weights of which had been determined by applying the hypothesis of Avogadro.   He said:

"When the body cannot be decomposed, it is necessary to conclude that the molecules of it consist of one substance throughout.   If the body is a

---

[1] " Faraday Lecture," *C. S. Journal*, [2] **10**, p. 955; Ostwald's translation of *Sunto*, p. 7.
[2] *Sunto*, p. 7.   (All the references to *Sunto* are to the German translation.)

compound, it is analyzed, and the constant weight-relations of its constituents determined; the molecular weight is then divided into parts proportional to the relative weights of the components, and the result is the quantities of the elements contained in the molecule of the compound, referred to the same unit as is used for the expression of all molecular weights." [1]

The meaning of this statement is made clear by a table of which the following is a portion.

Name of substance.	Weight of a volume, or molecular weight referred to the weight of a semi-molecule of hydrogen as unity.	Weights of the constituents of a volume, or a molecule, the sum being referred to the weight of a semi-molecule of hydrogen as unity.
Hydrogen	2	2
Ordinary oxygen ...	32	32
Phosphorus.........	124	124
Hydrochloric acid...	36·5	35·5 chlorine + 1 hydrogen
Water..	18	16 oxygen + 2 "
Calomel..	235·5	35·5 chlorine + 200 mercury
Corrosive sublimate..	271	71 " + 200 "
Carbon monoxide ...	28	16 oxygen + 12 carbon
Carbonic acid	44	32 " + 12 "
Alcohol.	46	6 hydrogen + 16 oxygen + 24 carbon
Ether.	74	10 " + 16 " + 48 "

Tables similar to that just given were arranged by Cannizzaro for several compounds of the same element; here is one of them.

Name of substance containing chlorine	Weights of chlorine in the molecules, referred to the weight of a semi-molecule of hydrogen as unity.
Hydrochloric acid	35·5 = 35·5
Chlorine	71 = 2 × 35·5
Mercuric chloride	71 = 2 × 35·5
Arsenious chloride	106·5 = 3 × 35·5
Stannous chloride	71 = 2 × 35·5
Stannic chloride	142 = 4 × 35·5
etc., etc., etc.	= n × 35·5

Atomic weight of chlorine = 35.5.

"By comparing the different quantities of one and the same element," Cannizzaro said, "which are contained either in the molecule of the free element, or in the molecules of its compounds, the following law stands out in relief: *the different weights of one and the same element contained in the various molecules are always whole multiples of one quantity, which is justly called the atom because it invariably enters the compounds without division.*" [2]

[1] Translated from Ostwald's German edition of *Sunto*, p. 8.
[2] *Sunto*, p. 10.

The *law of atoms*, thus enunciated by Cannizzaro, included the law of multiple proportions and the law of combining volumes.

"In order to determine the atomic weight of any element," Cannizzaro said, "it is essential to know the molecular weights, and the composition, of all or most of its compounds."[1]

Cannizzaro showed that it is possible to determine the atomic weight of an element whose molecular weight is unknown. Taking the case of carbon, he gave the following data.[2]

Name of carbon compound.	Molecular weight, referred to the atom of hydrogen.	Weights of the constituents, referred to the weight of an atom of hydrogen as unity.			Formulæ, taking $H=1$, $C=12$, $O=16$, $S=32$.
Carbon oxide...	28	12 carbon	$+16$ oxygen		CO
Carbonic acid..	44	12 "	$+32$ "		CO_2
Carbon sulphide	76	12 "	$+64$ sulphur		CS_2
Marsh gas......	16	12 "	$+4$ hydrogen		CH_4
Ethylene......	28	24 "	$+4$ "		C_2H_4
Propylene.....	42	36 "	$+6$ "		C_3H_6
Ether.........	74	48 "	$+10$ "	$+16$ oxygen	$C_4H_{10}O$

"If the molecular weight of carbon were known, it might be included in the series of the molecules of carbon compounds; but no greater advantage would be gained by doing this than by placing another compound in the list; for it would be merely a confirmation of the fact that the weight of carbon in any molecule which contains carbon is 12 or $n \times 12 = C_n$, where n is a whole number."[3]

Having given definite and quantitative meanings to the terms *molecule* and *atom*, and shown how to determine the relative weights of both kinds of particles, Cannizzaro proceeds to discuss the question whether it is better to express the composition of a molecule as a function of the molecules of its components, or to express the compositions both of the molecule itself and its components in terms of atoms. For instance, he asks; is it better to express in the formula of hydrochloric acid that a molecule of this compound contains a semi-molecule of hydrogen and a semi-molecule of chlorine, or an atom of hydrogen and an atom of chlorine? If the first method were adopted, the formula of hydrochloric acid would be written $H_{\frac{1}{2}}Cl_{\frac{1}{2}}$, where **H** and **Cl** represent a molecule of hydrogen and chlorine, re-

---

spectively; if the second method is used, the formula is HCl, where H and Cl represent atoms of the elements.

The drawbacks to the first method of expression are summarized by Cannizzaro. The molecular weights of many elements cannot be determined, because the elements are not gasifiable. If the vapour-densities, and therefore the molecular weights of the allotropic forms of oxygen and of sulphur are really different, the compounds of these elements would each have two or more formulæ, according as the quantities of their constituents were referred to this or that allotropic form of sulphur and oxygen. As the molecules of similar substances, of sulphur and of oxygen for instance, do not contain equal numbers of atoms, the formulæ of corresponding compounds would be dissimilar; on the other hand, if the compositions of molecules are expressed in atoms of their constituent elements, analogous compounds are found to have equal numbers of atoms in their molecules.

Cannizzaro based his system of formulæ on the expression of the compositions of molecules in terms of their constituent atoms. He said:

"The atom of every element is expressed by that quantity of it which invariably enters as a whole into equal volumes of the simple substance and its compounds; this quantity may be either the whole quantity contained in a volume of the free element, or it may be a fraction thereof."

Cannizzaro applied the system he had constructed, by using the hypothesis of Avogadro, to the expression of the compositions of various classes of compounds. To illustrate his methods and results, I will give a sketch of his treatment of the chlorides and iodides of mercury and of copper.

As many chlorides, bromides, and iodides had been gasified before 1858, there was no difficulty in finding the molecular weights of several of these compounds. But, in order to determine whether the weight of the other element which combined with chlorine, bromine, or iodine to form a molecule of a chloride, a bromide, or an iodide was the weight of one, two, three, or n atoms of that element, it was necessary to compare the compositions of many other molecules containing the element in question. The vapour-densities and analyses of the two

chlorides of mercury led Cannizzaro to the molecular formulæ HgCl and $HgCl_2$, and to the value 200 for the atomic weight of mercury, on the assumption that the weight of mercury in a molecule of either chloride is the weight of one atom of mercury. This value was confirmed by the consideration that the molecules of the two iodides of mercury, and also the molecules of certain gasifiable organic compounds of mercury, contain each 200 parts by weight of mercury. A further confirmation of the conclusion that the atomic weight of mercury is 200 was obtained by showing that the number obtained by multiplying the specific heat of mercury by 200 is very nearly the same as the products of multiplying the specific heats of bromine and iodine by 80 and 127 respectively, which numbers are the values obtained for the atomic weights of these elements from determinations of the vapour-densities and compositions of many of their compounds. Cannizzaro's value for the atomic weight of mercury was also confirmed by him, by finding that the quantities of heat required to raise molecular weights of the two chlorides, and of the two iodides of mercury, through equal intervals of temperature, are proportional to the numbers of atoms in the molecules of these compounds, if the molecular formulæ are taken to be HgCl, $HgCl_2$, HgI, and HgI_2, and the atomic weight of mercury to be 200.

As the vapour-density of mercury showed the molecular weight of that element to be 200, and as he had proved the atomic weight of mercury to be 200, Cannizzaro concluded that the molecule of this element is undivided in chemical reactions. He also pointed out that the weights of gaseous mercury, chlorine, hydrogen, and hydrochloric acid which occupy equal volumes are expressed by the formulæ Hg, Cl_2, H_2, and HCl.

No chloride or iodide of copper had been gasified. The similarities between the chlorides of copper and those of mercury suggested to Cannizzaro the molecular formulæ CuCl and $CuCl_2$ for the two chlorides of copper; analyses showed that 63 parts by weight of copper are combined with $35 \cdot 5$ parts by weight, that is, with one atom of chlorine in one chloride, and with 71 parts by weight, that is, with two atoms of chlorine in the other chloride. Hence, Cannizzaro said, the atomic weight

of copper is probably 63. This value was confirmed by determining the specific heat of copper and the specific heats of cuprous chloride and cuprous iodide, and reasoning on the data in the same manner as was done in the case of mercury and its compounds.

Cannizzaro did not attempt to decide whether the atomic weight of copper is identical with the molecular weight of that element, whether the quantity of the element which enters the molecule of compounds of it without division is a whole molecule or a fraction of a molecule of copper; for he recognized that there was no way of deciding the question so long as the vapour-density of copper was unknown.

The chemical similarities between hydrochloric acid, mercurous chloride, and the chlorides of potassium, sodium, lithium, silver, and gold inclined Cannizzaro to regard the compositions of the molecules of these compounds as similar. Knowing the molecular formulæ of the first and second members of this series to be HCl and HgCl respectively, he argued that the molecular formulæ of the other chlorides were probably KCl, NaCl, LiCl, AgCl, and AuCl; from these formulæ, taken with the results of analyses of the compounds, he deduced values for the atomic weights of potassium, sodium, lithium, silver, and gold, and he confirmed these values, and also the molecular formulæ he had given to the chlorides, by considerations based on the specific heats of the elements and the compounds.

The latter part of Cannizzaro's memoir deals with the classification of chemical reactions, and the representation of them as interchanges of atoms and groups of atoms. Most of this part of his essay is based on the notion of the equivalency of atoms and groups of different kinds; the subject is treated by Cannizzaro in the most lucid and suggestive manner. The consideration of this part of Cannizzaro's memoir must be deferred until I come to the subject of chemical equivalency in Chapter X.

When Cannizzaro had stated the *law of atoms*, that "the quantities of an element contained in different molecules are whole multiples of one and the same quantity," he said that objections might be raised to the method whereby molecular weights were determined by him, on the ground that it was too hypothetical. To that objection he replied: "If the compositions of equal volumes of substances, in the gaseous state, are compared under

the same conditions, it will be impossible to escape the following law: *all the different weights of one and the same element which are contained in equal volumes, whether of the free element or its compounds, are whole multiples of one and the same quantity.* In other words, every element has a special numerical value, by which, with the aid of integral coefficients, the gravimetric compositions of equal volumes of the various compounds of the element can be expressed. As all chemical reactions occur between equal volumes, or whole multiples of equal volumes, so all chemical reactions can be expressed by these numerical values and integral coefficients." [1]

Attempts have been made, in the last twenty or thirty years, to develope a system of expressing chemical reactions without the aid of the molecular and atomic theory. It is interesting to observe the revival of the method described by Cannizzaro, in the words quoted above, in one of the most suggestive of recent text-books. In his *Grundlinien der anorganischen Chemie* (published in the latter part of 1900) [2] Ostwald uses the terms *normal weight* and *molar weight* to express the ratio of the weight of any gas to that of an equal volume of a hypothetical gas, 32 times lighter than oxygen, called by him the *normal* gas; [3] he says that a *combining weight* may be attached to every substance; that all chemical reactions occur between weights which can be expressed by these combining weights or rational multiples of them; [4] and that combining weights are determined so that a whole number of them is always present in all normal or molar weights. [5]

Dumas said, in 1836, that the statement, "equal volumes of gases contain equal numbers of molecular or atomic groups," would be accepted by every one, but would advantage nothing; it would be but another hypothesis, another of those guesses whereof chemistry had already too many. Dumas was wrong: the hypothesis, which "would be of no use to anyone at present," did more to advance accurate knowledge than the facts to which Dumas besought chemists to return. Dumas was right: he himself returned to facts, and the results of his experiments enabled Cannizzaro, twenty years later, to throw a flood of light on the whole field of chemistry by re-stating the hypothesis which Avogadro had promulgated twenty five years before. Avogadro's hypothesis, interpreted and applied by Cannizzaro, proved to be a signal example both of the truth and the falsehood of the adage, "An ounce of fact is worth a pound of theory."

The dualistic system made too much of the superficial ex-

---

[1] *Sunto*, p. 12.
[2] An English translation appeared in 1902, with the title, *The Principles of Inorganic Chemistry*.
[3] *Grundlinien*, p. 92.
[4] *Grundlinien*, p. 147.
[5] *Grundlinien*, p. 148.

amination of reactions; most of the attempts to overthrow it looked too exclusively to composition. Cannizzaro studied both reactions and composition; he recalled chemists to the fundamental question of their science, "how changes occur in combinations of the unchanging." After Cannizzaro one might say, this substance is homogeneous because it acts thus, only when one added, this substance acts thus because it is homogeneous.

Dalton revived, supplemented, and used the atomic theory that had lain dormant for more than two thousand years, and the theory made clear the relations between many facts which had seemed unconnected. Cannizzaro applied the enlargement of the Daltonian theory made by Avogadro, and the facts which had accumulated during half a century fell into their proper places in an ordered sequence.

It is worthy of notice, as exemplifying the chemical genius of Berzelius, that but few of the atomic weights assigned by him to the elements were changed by using the hypothesis of Avogadro to find values for these magnitudes.

The influence of the teaching of Cannizzaro was soon apparent. In his *Lehrbuch der Organischen Chemie*, which appeared in 1861 (the preface is dated 1859), Kekulé used the atomic weights we use to-day ($O = 16$, $S = 32$, etc.), but he employed the vapour-densities of elements and compounds only as means of confirming the values for atomic and molecular weights which he deduced from comparing the reactions of compounds. The first edition of Lothar Meyer's *Modernen Theorien der Chemie* was published in 1864; Cannizzaro's treatment of the hypothesis of Avogadro is the foundation of the system of this book, which had a great influence on the advance of chemistry.

Hofmann's *Introduction to Modern Chemistry, Experimental and Theoretic*, appeared in 1865 (the first German edition was published in 1866). Hofmann laid the foundations of chemistry in the study of the weights of the combining volumes of gaseous elements and compounds, and the weights of the volumes of the gaseous products of chemical reactions; and he gradually led his readers to the conception of the molecule from which he deduced that of the atom. He used multiple proportions, combining proportions, and two-litre formulæ until he had estab-

lished his facts; then he translated these facts into the language
of molecules and atoms, basing this part of his teaching on the
hypothesis of Avogadro.

The *Chemical Society's Journal* for 1869 (**22**, 328) contained
a memoir by Williamson "On the Atomic Theory." William-
son's main objects were to prove the impossibility of expressing
the facts of composition, consistently and lucidly, by a system
founded only on determinations of equivalent or combining
weights, apart from the atomic theory; and to show that the
notion of groups of indivisible particles reacting as wholes arose
from the examination and comparison of chemical changes, and
every fact which made the existence of such atomic groups, or
molecules, more probable strengthened the theory of atoms.
Williamson endeavoured to determine the relative weights of
molecules by the laborious and inconclusive method of classifying
reactions and arranging compounds under certain types; he was
content to use the hypothesis of Avogadro only as a help, and to
confine its application to "perfect vapours," remarking that there
were discrepancies between the molecular weights determined
by chemical methods and those suggested by the use of the
Avogadrean rule.

Cannizzaro, in 1858, had advanced far beyond the point
reached by Williamson in 1869.

The discussion which followed the reading of Williamson's
memoir (see *C. S. Journal*, **22**, 433) degenerated into talk about
the finite or infinite divisibility of matter, a subject which
Williamson had set aside as not within the scope of his memoir.
Although the discussion took place nine years after Cannizzaro's
pamphlet came into the hands of chemists, no one showed any
grasp of the molecular and atomic theory; with the exception of
of the advice given by Brodie, to study the laws of gaseous com-
bination, no hint was given that the essential thing to do was to
determine the relative weights of molecules, and from the ap-
plications of the results to chemical reactions to construct a
method for finding the relative weights of atoms.

I have mentioned (p. 132) that both Laurent and Gerhardt
adopted. as the molecular weights of elements and compounds,
the weights of those quantities which occupied, in the gaseous

state, twice the volume occupied by a unit weight of hydrogen, except in those cases wherein this procedure led to formulæ containing fractions of atoms. If it is asserted that equal volumes of gases always contain equal numbers of molecules, then, these chemists said, the formulæ of ammonium chloride and sulphuric acid (to take two examples) must be written $N_{\frac{1}{2}}H_2Cl_{\frac{1}{2}}$ and $HS_{\frac{1}{2}}O_2$, unless values are given to the atomic weights of nitrogen, chlorine, and sulphur which are negatived by many facts.   To get over the difficulty, Laurent, and Gerhardt also, took the molecular weights of certain compounds to be the weights of volumes of them, as gases, equal to the volume of four unit weights of hydrogen.

Cannizzaro refused to accept the existence of any exceptions to Avogadro's hypothesis. In a short paper [1] published in 1857 Cannizzaro said: "I believe there are no exceptions to the universal law that equal volumes of gases contain equal numbers of molecules, and that the apparent exceptions will disappear when more searching experiments are made."

The material for showing that the apparent exceptions to Avogadro's generalization were not real exceptions had been supplied by Deville, in the note referred to by Cannizzaro; for Deville had shown that certain compounds are separated into their constituents by heat, the vapours of these compounds are mixtures of the constituents, and the compounds are again formed as the vapours cool. Investigations made at a later time showed that the vapour formed by heating ammonium chloride is a mixture of ammonia and hydrochloric acid, and the vapour formed by heating sulphuric acid is a mixture of sulphur trioxide and water. The observed densities of these vapours (and many similar cases have been observed and examined since 1857) were therefore the densities of mixtures; but Avogadro's generalization applies to homogeneous gases only.

Cannizzaro laid down the condition which must be observed

---

[1] *Della dissociazione ossia scomposizione dei corpi sotto l'influenza del calore;* M. H. Sainte-Claire Deville (*Compt. rendus,* 23d Nov. 1857, p. 857); *considerazioni di* S. Cannizzaro. (*Nuovo Cimento,* 6, 428 [1857]). Translations of this note, and another on the same subject published by the same author in 1858, are given in Ostwald's German edition of Cannizzaro's memoirs (*Klassiker der exakten Wissenschaften,* No. 30).

in applying Avogadro's generalization: proof must be forth-coming that the vapour whose density is determined is homoge-neous; and the fact that the original compound is obtained by cooling the vapour is not a sufficient proof of the homogeneity of the vapour.[1]

I do not make any attempt to trace the history of the inves-tigations of so-called abnormal vapour-densities. The subject of the separation of homogeneous substances by heat, and the re-formation of the original substances by cooling, will be glanced at, in dealing with the conditions of chemical equilibrium, in Chapter XV.

---

[1] An interesting pamphlet, entitled *Avogadro and Dalton: The Standing in Chemistry of their Hypotheses*, by Andrew N. Meldrum, was published in 1904 by William F. Clay [Edinburgh].

CHAPTER V.

THE DETERMINATION OF MOLECULAR WEIGHTS FOUNDED ON THE MEASUREMENTS OF CERTAIN PHYSICAL PROPERTIES OF DILUTE SOLUTIONS, AND THE EXTENSION OF AVOGADRO'S LAW TO SUCH SOLUTIONS.

IN the last chapter I traced the development of that conception of the molecule which led to the inclusion of the Daltonian atomic hypothesis in the more comprehensive atomic and molecular theory. So far as its chemical applications are concerned, that theory rests on the assumption that Avogadro's generalization—equal volumes of gases, equal numbers of molecules—is a statistically accurate description of facts, in terms of the hypothesis that matter has a grained structure.[1] Avogadro's law does not assert that the number of molecules in a determinate volume of any homogeneous gas is exactly the same as the number of molecules in the same volume of any other homogeneous gas; the law affirms that the numbers of molecules contained in those volumes of homogeneous gases which are equal at the same temperature and pressure are so nearly the same that the applications of the statement to chemical reactions are not materially affected by assuming perfect equality of numbers of molecules in equal volumes. The law put into the hands of chemists an instrument for determining the relative weights of the molecules of homogeneous gases with sufficient accuracy for the purpose for which these values were required. But the application of Avogadro's law was limited to those elements and compounds which could be obtained in the gaseous state; and neither chemists nor physi-

---

[1] The subject of the general kinetic theory of gases, which theory includes Avogadro's law as one special deduction from its fundamental assumptions, belongs to physics, and is outside the scope of this book.

cists could rest satisfied with that limitation. Physicists sought
to extend the molecular theory, and to bring within its grasp
homogeneous solids and liquids as well as gases; chemists
endeavoured to find a trustworthy method for determining the
relative weights of the ultimate particles which take part in
chemical reactions between non-gasifiable elements and com-
pounds. The most important chemical results of these labours
have been, an extension of the law of Avogadro which asserts
that, under definite and definable conditions, equal volumes
of certain solutions contain equal numbers of molecules of the
dissolved homogeneous substances, and the elaboration of
practicable methods for determining the relative weights of
the molecules of homogeneous substances in such solutions.

It is interesting to observe that the order of procedure in
the extension of the Avogadrean law followed lines broadly
similar to those along which the development of the atomic
theory advanced.

Many facts were known concerning the compositions of
compounds; to these, dalton boldly applied the atomic theory,
and order appeared where no order had been seen before. A
few years later, Avogadro extended the theory, and supplied
an instrument whereby most of the facts which remained out-
side the less comprehensive theory of Dalton might have been
brought into interdependence. But chemists overlooked the
generalization of Avogadro, and proceeded with the accumula-
tion of empirical facts; and, looking back, we may say that,
on the whole, they did wisely. Then came Cannizzaro, who
recalled and used the illuminating generalization of Avogadro.
The facts fell into their places in an orderly scheme, and new
paths of discovery were opened.

Facts of fundamental importance concerning the freezing-
points of solutions were observed and chronicled by Blagden
twenty years before the publication of Dalton's *New System*. But
it was not until the seventies of the next century that a begin-
ning was made, by de Coppet, in the application of the molecular
theory to these facts. The experimental data then increased
rapidly. Early in the eighties, Raoult expressed the facts
in a generalization which supplied the means for determining

the molecular weights of homogeneous substances in certain solutions. A few years later, van't Hoff included the empirical generalization of Raoult in a theory of dilute solutions; and both theoretical and empirical advance then became rapid.

The history of the connexions between the vapour-pressures of solutions and the quantities of the dissolved substances is broadly similar to that of the connexions between the freezing-points, and the contents of solutions.

I will now describe these two histories in some detail.

In 1788, Blagden made observations on the cooling of water below 32° F. without the formation of ice.[1] He extended his experiments to water containing salts, and acids, dissolved in it; and the results led him to examine the influence of various substances dissolved in water on the freezing-point of the solvent.[2]

The general conclusions which Blagden drew from the results of his determinations were these. The freezing-point of water is lowered by the solution therein of such compounds as common salt, salammoniac, green vitriol, and Rochelle salt. The amount of the lowering is generally proportional to the weight of the substance in a constant weight of the solvent; but the depression caused by such compounds as alkalis, oil of vitriol, spirit of salt, and spirit of wine, increases rather more rapidly than in strict proportion to the weight of the dissolved compound. When moderate quantities of two compounds, such as nitre and common salt, or salammoniac and common salt, are dissolved in water, the lowering of the freezing-point of the water is equal to the sum of the effects of the compounds acting separately; but, if a saturated solution of one of the compounds is used, then the lowering of the freezing-point of the water caused by the other compound increases more rapidly than in proportion to the weight of that compound.

In 1861, Rüdorff took up the examination of the connexions between the freezing-point of water and the quantities of salts dissolved in the water, apparently without knowing what had been done by Blagden seventy years before. Rüdorff's results

were published in three memoirs.[1]   His general conclusion was based on a large number of determinations; it was to the effect that the lowering of the freezing-point of water which is caused by dissolving a salt in the water is proportional to the weight of the salt in a constant weight of water, provided three assumptions are made, namely, some salts dissolve as anhydrous salts, others as hydrated salts, and others as anhydrous salts until a certain amount of depression of freezing-point is reached, after which the salts combine with water and dissolve as hydrated compounds.

Three memoirs on this subject were published by de Coppet [2] in the years 1871 and 1872.   He confirmed the law of proportionality, and extended it to supersaturated aqueous solutions, and he made an important advance by stating his results in the form of what he called *atomic depressions* of the freezing-point of water.   An atomic depression was calculated by de Coppet by multiplying the lowering of the freezing-point of water, caused by the solution in 100 grams thereof of 1 gram of a salt, by the atomic weight (we should now say the molecular weight) of the dissolved salt.   According to de Coppet, the atomic depressions caused by salts of the same class are nearly equal.

The main object of de Coppet was the investigation of "the chemical constitution of saline solutions."   He made many observations, and on these he based complicated calculations for the purpose of determining the quantity of each of the many hydrates of a salt which he assumed to exist in solution.

Raoult began his work on freezing-points by attempts to determine the strengths of various alcoholic liquors by measuring their freezing-points.[3]   He then made determinations of the effects of dissolving various alcohols in water on the freezing-point of the water; and about 1882 he passed to the consideration of the effects of organic compounds in general.[4]   In his memoir published in 1883, Raoult used dilute solutions (not more

[1] *Pogg. Annal.*, **114**, 63 [1861]; **116**, 55 [1862]; **145**, 599 [1872].
[2] *Annal. Chim. Phys.*, (4) **23**, 366 [1871]; **25**, 502 [1872]; **26**, 98 [1872].
[3] François Marie Raoult was born in 1830 and died in 1901.
[4] Various papers by Raoult appeared in *Compt. rendus.*   Those memoirs I have consulted are to be found in *Annal. Chim. Phys.*, (5) **28**, 137 [1883]; (6) **2**, 66 [1884]; (6) **4**, 401 [1885].

than one molecular weight in grams of substance in 1000 grams
of water) of various alcohols, phenols, aldehydes, ethers, amides,
amines, sugars, and organic acids.   He stated his results in two
forms: (1) *depression-coefficients*, that is, depression of the
freezing-point of water caused by the solution of one gram of
each compound in 100 grams of water; and (2) *molecular de-
pressions*, that is, depression-coefficients multiplied by the
molecular weights of the dissolved compounds.   The molecular
depressions observed by Raoult varied somewhat, but the value
was practically constant for all the members of the same class
of organic compounds.   He thought himself justified in con-
cluding that the molecules of organic compounds dissolved in
equal weights of water, such that dilute solutions are formed,
cause nearly equal depressions of the freezing-point of water.

Raoult said that all his results were described with sufficient
accuracy by supposing that the molecular depression caused by
an organic compound is the average of the depressions caused
by the atoms which compose its molecule, and the depression
caused by each atom depends on its nature, and is independent
of its position in the molecule.   He calculated the several
atomic depressions of carbon, hydrogen, oxygen, and nitrogen to
be 15, 15, 30, and 30.   Hence, he said, the molecular depression
of a compound $C_pH_qN_rO_s$ will be

$$\frac{(p\times15)+(q\times15)+(r\times30)+(s\times30)}{p+q+r+s}.$$

The most important outcome of the results chronicled in this
memoir (1883) was the establishment of what promised to be a
method capable of general application for finding the molecular
weight of an organic compound by determining the depression
of the freezing-point of water produced by dissolving the com-
pound in that solvent.   Raoult gives the following directions for
doing this: determine the simplest formula for the compound;
calculate the molecular depression = A;   determine the de-
pression-coefficient of the compound = a; then

$$\frac{A}{a}=\text{approximate molecular weight of the compound.}$$

Take the case of oxalic acid. The possible molecular formulæ (calculated from the results of analyses and the atomic weights of carbon, hydrogen, and oxygen) are $CHO_2 = 45$, $C_2H_2O_4 = 90$, $C_3H_3O_6 = 135$, etc. The calculated molecular depression is $\dfrac{15 + 15 + (2 \times 30)}{4} = 22\cdot5$ for CHO_2 and its multiples. The depression-coefficient of oxalic acid was found by Raoult to be $0\cdot255$; hence mol. weight $= \dfrac{22\cdot5}{\cdot255} = 88\cdot3$.

The formula $C_2H_2O_4$ requires the value 90; hence $C_2H_2O_4$ is the molecular formula of oxalic acid.

In order to bring within the scope of the molecular theory his generalization that the molecules of organic compounds cause nearly equal depressions of the freezing-point of water, Raoult supposed (in 1883) that the act of dissolution separates the molecules of the dissolved compound, as molecules are separated by vaporization, and the separated molecules affect the physical properties of water in a way which is independent of their composition and is conditioned only by their number.

In the memoir of 1884, Raoult showed that the connexion between the molecular weight of a compound and the depression of the freezing-point of water, caused by the solution of the compound in that solvent, probably holds good for all solidifiable solvents. The law was expressed by Raoult as follows:

$$Ma = T, \quad \text{or} \quad M = \frac{T}{a},$$

where M = molecular weight, T = molecular depression, and a = depression-coefficient.[1]

Raoult determined the depression-coefficients of about 60 organic compounds dissolved in acetic acid, about 10 compounds dissolved in formic acid, about 60 compounds in benzene, about

---

[1] Raoult used solutions so dilute that 2000 grams of the solvent contained less than one molecule of the dissolved compound measured in grams. By using solutions so dilute, Raoult says that (1) a fair quantity of the solvent may freeze without sensibly changing the concentration of the solution, hence the thermometer remains steady for some time; and (2) most of the errors are avoided which result from the somewhat arbitrary assumptions made concerning the number of molecules of the solvent which may combine with the dissolved compound.

20 in nitrobenzene, and about 8 in ethylene dibromide; he also made determinations with aqueous solutions of 14 acids, 3 caustic alkalis, 11 chlorides, bromides, and iodides, and 43 inorganic salts, mostly salts of oxyacids. The molecular depressions of the organic compounds in each organic solvent approached one of two values, of which one was approximately double the other; these values were, 39 and 18 for acetic acid, 28 and 14 for formic acid, 49 and 25 for benzene, 72 and 36 for nitrobenzene, and 118 and 58 for ethylene dibromide. The maximum molecular depression of the freezing-point of water caused by salts not decomposed by that solvent was 47; but most of the numbers for aqueous solutions of salts approached one or other of the values 37 and $18 \cdot 5$.

Raoult's law for finding the molecular weight of a homogeneous substance (see p. 150) now took the following form:

$$M = \frac{K}{a},$$

where M = molecular weight, a = depression-coefficient, and K = a constant which expresses the depression of the freezing-point of the particular solvent caused by the solution of one molecular weight of a homogeneous substance in that solvent. Raoult's results indicated that K had two values for each solvent; further investigations were required to explain these results.

Raoult brought his results within the scope of the molecular theory by using the distinction between the physical and the chemical molecule. He concluded that all physical molecules, of whatever kind, depress the freezing-point of a solvent by the same amount when dissolved in a constant weight of that solvent. He supposed that the molecular depression reaches its maximum value when the physical molecules are completely separated, as they are in a perfect gas, and each is identical with a single chemical molecule; but if some of the chemical molecules are united in pairs, then the molecular depression is less than the maximum, because each double molecule (each physical molecule) produces no greater effect on the freezing-point of the solvent than one simple (chemical) mole-

cule: if all the chemical molecules are united in pairs, the molecular depression is half its maximum value.

In order to throw light on the results which showed that the molecular depressions produced by the same compound are not the same for different solvents, Raoult divided the maximum molecular depression observed for each solvent by the molecular weight of that solvent, and obtained numbers which expressed the depressions caused by the solution of one molecule of a compound in 100 molecules of a solvent.

His results were as follows:

Solvent.	Depression of freezing-point caused by the solution of one molecule of a compound in 100 molecules of the solvent.
Water...	$2 \cdot 61°$
Formic acid...................................	$\cdot 63°$
Acetic acid....................................	$\cdot 65°$
Benzene..	$\cdot 64°$
Nitrobenzene.................................	$\cdot 59°$
Ethylene dibromide..........................	$\cdot 63°$

Considering that the action, of whatever character it may be, between the molecules of the dissolved compounds and those of the solvent is independent of the composition of the molecules of the compound in solution, one would suppose, Raoult said, that the action would also be independent of the composition of the molecules of the solvent. Raoult regarded the results tabulated above as confirming this supposition for all the solvents he had examined except water. To explain the apparent anomalies in the case of water, Raoult supposed that each physical molecule of water is composed of several chemical molecules held in union. If the maximum molecular depression for water is taken to be 37, and it is assumed that a physical molecule of water is composed of three chemical molecules of $H_2O (=18)$, then $\frac{37}{18 \times 3} = \cdot 685$. But a molecular depression of 47 was observed in certain aqueous solutions; assume that the physical molecule of water is composed of four chemical molecules, and we have $\frac{47}{4 \times 18} = \cdot 65$. Hence Raoult's *general law of the freezing of solvents:* if one molecule of any substance is dissolved in 100 molecules of any liquid, which is

not the same as the dissolved substance, the freezing-point of the liquid is depressed by an amount which is always nearly the same, and approaches ·63°.

A report on Raoult's work (by Cahours, Berthelot, and Debray) was presented to the French Academy in 1883.[1] The reporter (Debray) thought that Raoult's observations were not sufficient to justify his *general law of the freezing of solvents*. In his memoir of 1885, Raoult added many observations to those he had already chronicled of the influence of salts on the depression of the freezing-point of water, and announced that he had "sensibly modified his first impression." In this memoir, Raoult divided the measurements into groups, and classified the salts which he used, in accordance with (1) the valencies of their metals, and (2) the basicities of their acids. By doing this, Raoult attempted to deduce values for the depressions of the freezing-point of water due to the acid radicals of the salts, and values due to the metals of the salts he employed. He said: "These results prove that . . . the general law does not apply to dissolved salts; on the contrary, they tend to indicate that it is applicable to the constituent radicals of the salts, almost as if these radicals were simply mixed in the solutions." Raoult explained the anomalous results which were observed in many cases by supposing that condensation occurred of two, three, or more radicals, or metals, into groups which acted as single (physical) molecules, and he considered the physical molecules of water to consist of groups of chemical molecules.[2]

But Raoult did not arrive at such a clear conception of the actions which result in the depression of the freezing-point of water, by the solution of salts in that solvent, as could be applied, directly and quantitatively, to every special case.

Raoult had enriched chemistry with a means of finding the molecular weights of compounds, which was certainly applicable to organic compounds dissolved in other compounds of carbon. But the anomalous results he had obtained with aqueous solu-

---

[1] *Compt. rendus*, October 15, 1883.
[2] Later investigations have shown that Raoult's *general law of the freezing of solvents* is not an accurate description of the facts.

tions stood in the way of the general adoption of his method. An extension of the molecular theory was demanded which should cover the apparent anomalies simply and fully, and point the way to new investigations.

Let us now trace the main lines along which knowledge has advanced of the connexions between the vapour-pressures of solutions and the molecular weights of the dissolved substances.

To determine the boiling-point of water is to determine the temperature whereat the pressure of the vapour of water is equal to the pressure of the atmosphere. It has been known for a long time that aqueous solutions of non-volatile substances boil at temperatures which are higher than the boiling-point of pure water. This fact may be expressed in two ways: one may say that the temperature to which the solution of a non-volatile substance in water must be raised, in order that the pressure of the aqueous vapour coming from the solution shall be equal to the pressure of the atmosphere, is higher than the temperature to which pure water need be raised in order to fulfil that condition; or one may say that the vapour-pressure of water, at any determinate temperature, is lowered by dissolving a non-volatile substance in the water. Hence the connexions between the boiling-points of aqueous solutions of non-volatile substances and the contents of these solutions may be investigated by measuring either the temperatures of the solutions at equal pressures, or the pressures of the aqueous vapour at equal temperatures. The former method was used by most of the earliest workers in this field; the latter method was employed by Gay-Lussac and by those who came after him; and both methods have been used in recent years.

In 1886, Raoult extended the investigation of the connexions between the boiling-points and the contents of solutions to solvents other than water, and advanced the subject very notably. The most important general results of the experiments made before the behaviour was studied of solutions in solvents other than water, were these.[1]

---

[1] The chief memoirs on the subject are: (1) von Babo, *Jahresbericht* for 1848–9, **11**, 93; for 1859, 72. (2) Wüllner, *Pogg. Annal.*, **103**, 529 [1858]; **105**, 85 [1858]; **110**, 564 [1860]. Tammann, *Wied. Annal.*, **24**, 523 [1885]. (3) Ostwald,

The ratio between the vapour-pressure of water and the vapour-pressures of aqueous solutions of many salts is independent of temperature, within a certain range of temperature; but in some cases the ratio varies with the temperature, sometimes increasing and sometimes decreasing as temperature increases.

The depression of the vapour-pressure of water, which is caused by the solution of a salt in water, is very often proportional to the weight of the salt dissolved, but this statement is not an accurate description of every case.

Raoult [1] measured the depressions of the vapour-pressure of ether at a constant temperature produced by dissolving different weights of each of five organic compounds in ether. The organic compounds were, terpene (boiling-point 160°), nitrobenzene (b.-p. 205°), aniline (b.-p. 182°), methyl salicylate (b.-p. 222°), and ethyl benzoate (b.-p. 213°). His results proved that the depression of the vapour-pressure of ether is exactly proportional to the number of molecules of the dissolved compound, provided that number is not less than about 2, nor more than about 15, in 100 molecules of the solvent. He then made experiments on the influence of temperature on the connexion between the depressions of the vapour-pressure of ether and the molecular concentrations of ethereal solutions of the compounds metioned above, and found that the relation is the same at all temperatures between 0° and 21°. Raoult confirmed the conclusion he had drawn by extending his determinations to 13 organic compounds, whose molecular weights and boiling-points differ considerably, and one inorganic compound (antimony trichloride). He then examined solutions of various compounds in 11 different solvents, namely, water, phosphorus trichloride, carbon disulphide, carbon tetrachloride, chloroform, amylene, benzene, methyl iodide, methyl bromide, acetone, and methyl alcohol. The results confirmed the statement that the depression of the vapour-pressure of the solvent is proportional to the number of molecules of the dissolved sub-

Lehrbuch der Allgemeinen Chemie, I, 405 [1st ed. 1885].   (4) Emden, *Wied. Annal.*, **31**, 145 [1887].
[1] *Compt. rendus*, **103**, 1125 [1886]; **104**, 1430 [1887]; *Zeitsch. für physikal. Chemie*, **2**, 353 [1887].

stance, provided that number is not more than about 10 to 15 per 100 molecules of solvent.

It is evident that Raoult's results made it possible to calculate the molecular weight of a homogeneous substance from determinations of the vapour-pressures of a solvent whose molecular weight is known, and a solution (of about 10 per cent. molecular concentration) of the substance in that solvent. The ratio between the vapour-pressure of a solvent, and the depression thereof caused by the solution of a homogeneous substance, was found by Raoult to be equal to the ratio between the sum of the number of molecules of the dissolved substance and solvent and the number of molecules of the dissolved substance. Putting p = vapour-pressure of solvent, p' = vapour-pressure of solution, n = number of molecules of dissolved substance, and N = number of molecules of solvent, Raoult's generalization states that

$$\frac{p-p'}{p} = \frac{n}{N+n}.$$

This statement may be put into different forms for the purpose of calculating the molecular weight of the dissolved substance; perhaps the simplest form is the following:

Mol. wt. of dissolved substance =

$$\frac{\left(\dfrac{\text{100 gr. solvent} \times \text{mol.wt. of solvent}}{100}\right) \times \left\{\begin{array}{l}\text{vap. press.}\\\text{of solvent}\end{array}\right\}}{\text{depression of vapour-pressure of solvent}}.$$

It should be noticed that Raoult made only one determination of the depression of the vapour-pressure of water caused by the solution of a salt therein. Considering that the results of the determinations made by other observers who used water as the solvent were not nearly so uniform as those obtained by Raoult, it is not justifiable to apply Raoult's law to aqueous solutions of salts.

It is more convenient to determine the increase of the boiling-point of a solvent than to measure the depression of its vapour-pressure caused by the solution of a determinate weight of a

homogeneous substance in the solvent. It is customary to determine the *molecular increase of boiling-point* of a solvent by experiments with solutions of a substance whose molecular weight is known, and then to calculate the molecular weight of the substance for which this information is required by using the equation

mol. weight of dissolved substance =

$$\text{mol. raising of b.-p.} \times \frac{\text{grams substance dissolved in 1 mol. solvent}}{\text{observed rise of b.-p. of solvent}}.$$

The history of the practical details of the application of Raoult's law to the determination of molecular weights does not come within the scope of this book.

Definite connexions had been established between the depressions of the freezing-points of many solvents and the numbers of molecules of the dissolved substances on the one hand, and between the depressions of the vapour-pressures (or the increments of the boiling-points) of many solvents and the numbers of mloecules of the dissolved substances on the other hand. By reasoning based on the dynamical theory of heat, Guldberg [1] showed (in 1870) that the depression of the freezing-point and of the vapour-pressure of water, caused by the solution of a homogeneous substance in that solvent, must be proportional. In 1878 Raoult [2] established this proportionality on an experimental basis by determining and comparing the numerical values of the depressions of the freezing-point and the depressions of the vapour-pressure of water caused by 18 salts. His results showed that the depression of vapour-pressure caused by any one of these salts was approximately equal to the depression of freezing-point multiplied by a constant (about 7·6).

It was shown by van't Hoff,[3] in 1887, by thermodynamical reasoning, that Raoult's law of depression of vapour-pressure is causally connected with the laws of osmotic pressure of solutions. As Guldberg had proved theoretically, and Raoult had established

[1] *Compt. rendus*, **70**, 1349 [1870].

[2] *Ibid.,*, **87**, 167 [1878].

[3] *Zeitsch. für physikal. Chemie*, **1**, 494 [1887].

experimentally, that the depression of the freezing-point is proportional to the depression of the vapour-pressure of a solvent caused by the solution therein of the same compound, van't Hoff concluded that the osmotic phenomena of solutions must be connected with the freezing-points of the solutons in the same way as they are connected with the vapour-pressures of the solutions. By thermodynamical reasoning (which is not within the scope of this book),[1] van't Hoff deduced an expression for Raoult's empirical constant K, that is, for the molecular depression of the freezing-point of any particular solvent (see p. 151), in terms of the freezing-point and the heat of fusion of the solvent. The expression is

$$K = \frac{2T^2}{100L}, \quad \text{or} \quad K = \frac{\cdot 02T^2}{L},$$

where T = freezing-point of the solvent in absolute temperature, and L = heat of fusion of the solvent.

The following table presents a comparison of the values of K calculated by van't Hoff, for 5 solvents, with those established by experiment. [2]

Solvent.	Freezing-point (T).	Heat of fusion (L).	$\frac{\cdot 02T^2}{L}$	K.
Water.	273°	79 thermal units	18·9	18·5
Acetic acid.	273°+16·7°	43·2 " "	38·8	38·6
Formic acid.	273°+ 8·5°	55·6 " "	28·4	27·7
Benzene.	273°+ 4·9°	29·1 " "	53	50
Nitrobenzene.	273°+ 5·3°	22·3 " "	69·5	70·7

In a note to a memoir by Beckmann, Arrhenius[3] deduced an expression for the connexion between the molecular depression of the vapour-pressure of a solvent, the boiling-point, and the heat of vaporization of the solvent, which is similar to

[1] The student may consult van't Hoff's memoir in *Zeitschr. für physikal. Chemie*, **1**, 481 (a translation will be found in *Phil. Mag.*, (5) **26**, 81 [1888]), and Ostwald's *Solutions*, pp. 221–226.

[2] The experimental values differ slightly from the maximum values given by Raoult in his memoir of 1884. When van't Hoff's memoir was published, the heat of fusion of ethylene bromide was unknown; from the experimental value of K = 118 for ethylene bromide, van't Hoff calculated the heat of fusion of that compound to be 13, and he adds that Pettersson privately communicated that he had determined the value to be 12·94.

[3] *Zeitsch. für physikal. Chemie*, **4**, 550.

that given above, substituting boiling-point for freezing-point and heat of vaporization for heat of fusion.

The theoretical proofs which were given by van't Hoff of the facts, experimentally established by Raoult, that the depressions of the freezing-points and of the vapour-pressures of many solvents which are caused by the solution of homogeneous substances in these solvents are dependent only on the number, and not on the composition of the molecules of the dissolved substance, provided the solutions are dilute, rested on the demonstration of a causal connexion between the depressions in question and the osmotic pressures of the solutions. It is necessary, then, to glance at the history of the conception of osmotic pressure.

About the middle of the eighteenth century, the Abbé Nolet described experiments, which showed that, if a bladder is tied over the mouth of a glass vessel which is filled with spirit of wine, and the vessel is immersed in water, liquid passes into the vessel and the bladder is expanded.[1] Facts similar to this were observed and chronicled by various naturalists during the first half of the next century: these facts proved that the particles of two miscible liquids tend to pass the one into the other until they are perfectly equally distributed; if the liquids are separated by a membrane which is permeable only by one of them, a pressure is exerted on the membrane by the other liquid; if one of the liquids is a solution of a substance the particles of which cannot pass through the membrane, and the other liquid is the pure solvent, which itself is able to permeate the membrane, a pressure is exerted by the solution on the membrane. In 1867, Traube[2] endeavoured to measure the *osmotic*[3] *pressures* exerted by aqueous solutions by placing a membrane, which was intended to be quite impermeable by the dissolved substance, between the solution and water; but Traube did not succeed in preparing membranes which were perfectly impermeable by the substances solutions whereof he examined. In 1877, Pfeffer[4] prepared membranes which were

---

[1] *Leçons de Physique expérimentale, par M. l'Abbé Nolet* [Amsterdam, 1754].
[2] *Archiv. für Anat. und Physiol.* for 1867, p. 87.
[3] The term *osmotic* is derived from ὠσμός = impulsion.
[4] *Osmotische Untersuchungen*, Leipzig, 1877.

practically impermeable by certain substances in aqueous solution. His measurements showed that the pressures exerted by these solutions depended on the nature of the substances in solution. A series of measurements led to the conclusion that the pressures of aqueous solutions of cane-sugar were approximately proportional to the concentration, and also to the temperature of the solution. In 1884, H. de Vries compared the osmotic pressures of aqueous solutions of various compounds by immersing in them the cells of certain plants, and determining the concentrations of the solutions when these were in osmotic equilibrium with the contents of the cell.[1] Solutions whose osmotic pressures are equal were said by de Vries to be *isotonic* (ίσος = equal, and τονος = stretching). The general results of de Vries' measurements were: (1) the osmotic pressures of a solution are proportional to the concentration of the dissolved substance; (2) equimolecular solutions of the organic compounds he examined exerted equal osmotic pressures; (3) equimolecular solutions of similar salts (for instance, salts of nivalent metals with monobasic acids), possess equal osmotic pressures.[2] Donders and Hamburger [3] (in 1889–90) used a method similar to that employed by de Vries, and proved that solutions which are isotonic at 0° are also isotonic at 34°: as Pfeffer had shown that osmotic pressure increases as temperature increases, it followed that this increase is independent of the nature of the dissolved substance.

Tammann (in 1888) determined the equality of the osmotic pressures of two aqueous solutions by an optical method, and the concentration of the liquids when they were isotonic (or

---

[1] The membranes of these cells are permeable by water but not by the substances solutions of which were used: if the exterior solution had a greater osmotic pressure than that of the contents of the cell, the protoplasm contracted and was detached from the cell-wall; if the osmotic pressure of the solution was equal to, or less than that of the cell, the protoplasm clung closely to the cell-wall. By gradually diluting a solution, it was possible to find the concentration at which the osmotic pressure of the solution was equal to that of the contents of the cell; a similar process was then performed for another solution; the osmotic pressures of the two solutions were now equal, because the pressure of each was equal to that of the contents of the cell.

[2] The results of a second and third series of measurements by de Vries were published in *Zeitsch. für physikal. Chemie*, **2**, 415 [1888]; and **3**, 103 [1889].

[3] See *Zeitsch. für physikal. Chemie*, **6**, 319 [1890].

isomotic, to use Tammann's expression).[1]   Tammann's results showed that the ratio of the concentrations whereat two solutions of salts exhibited equal osmotic pressures did not change much as dilution increased.   Equimolecular solutions of the organic compounds examined showed osmotic pressures which were equal within the limits of experimental error.

Tammann drew attention to the fact that the vapour-pressures of isotonic solutions are equal.

In 1891, Adie [2] published the results of direct measurements of the osmotic pressures of saline solutions made by the method introduced by Pfeffer.   His results showed a rough proportionality between concentration and osmotic pressure.   But if the ordinary formulæ of the salts used were regarded as molecular formulæ, then Adie failed to trace any general connexion between the numbers of molecules in solution and the osmotic pressures of that solution at different concentrations.

It has not been customary of late years to attempt direct measurements of the osmotic pressures of solutions for chemical purposes, because determinations can be made of the depressions which are produced in the vapour-pressures and in the freezing-points of solvents by dissolving homogeneous substances therein both more easily and more accurately than measurements of osmotic pressures.   And since the theory of dilute solutions has been established by van't Hoff, and extended by Arrhenius to include all the cases which at first seemed to be anomalous, it has become possible to calculate the osmotic pressures of dilute solutions, should it be necessary to know these values, from measurements of freezing-points and of boiling-points.   The subject of the osmotic pressures of solutions has been absorbed in a general theory which supplies the chemist with more serviceable and workmanlike instruments than those he was obliged to use when he attempted to make direct determinations of osmotic pressures.

---

[1] *Wied. Annal.*, **34**, 299 [1888].   If two aqueous solutions which are separated by a membrane are of different concentrations, water flows in one direction or the other, the concentrations of the solutions change, and this is accompanied by changes of the refractive powers of the solutions.   Tammann adjusted the liquids so that no change occurred in the refractive power of either; the liquids had then the same osmotic pressure.

[2] *C. S. Journal*, **59**, 344 [1891].

In 1902 and 1905, Morse and Frazer succeeded in making membranes in porous pots, which were capable of sustaining considerable pressures and were quite impermeable by cane sugar.[1]

The memoir of van't Hoff, already referred to, is of fundamental importance.[2]

"Imagine a vessel," van't Hoff said, " completely filled with an aqueous solution of sugar and immersed in water. If the solid walls of the vessel are permeable by water, but not by sugar in solution, the attraction of the sugar-solution for water will cause water to enter the vessel; but the inflow of water will soon reach its limit, because of the pressure which follows the entrance of even a very small quantity of water. Under these conditions, equilibrium is established, and a pressure, which we shall call *osmotic pressure*, is exerted on the walls of the vessel."

The object of van't Hoff's memoir was to elucidate the analogies, amounting, he said, almost to identity, between the osmotic pressures of solutions and the pressures of gases. If the vessel which is filled with the solution of sugar were furnished with a piston, the pressure on the vessel could be increased or decreased by depressing or releasing the piston, and each change of pressure would be accompanied by a change of the concentration of the sugar-solution, inasmuch as water would flow, outwards or inwards, through the walls of the vessel. The change of pressure and of concentration effected by movements of the piston is exactly analogous to the rarefaction or the condensation of a gas, except that in the first case the concentration is altered by the outflow or inflow of the solvent through the *semi-permeable*[3] walls of the vessel. A process of this kind can be made reversible if the pressure of the piston is made equal to the opposing pressure, which, in the case of solutions, is the osmotic pressure. Hence the second law of thermodynamics can be applied to the phenomena.

The first deduction arrived at thermodynamically by van't Hoff was, that the concentration of a very dilute solution is proportional to the osmotic pressure. The equivalent of this statement applied to gases is known as Boyle's law. This theoretical

---

[1] *American Chemical Journal*, **28**, 1 [1902]; **34**, 1 [1905].

[2] *Zeitsch. für physikal. Chemie*, **1**, 481 [1887]; translation in *Phil. Mag.*, (5) **26**, 81 [1888].

[3] The expression, a *semi-permeable membrane*, which is constantly used in memoirs on osmotic pressure, means a membrane permeable by a solvent but not by the substance dissolved therein.

deduction is well confirmed by the experimental results obtained by Pfeffer and by de Vries, which have been described (pp. 159, 160). The second deduction made by van't Hoff was, that osmotic pressure is proportional to absolute temperature when concentration is constant. A large probability was established in favour of this generalization by data which were obtained experimentally by Pfeffer and by Donders and Hamburger (see pp. 159, 160), and also by the results of experiments made by Soret.[1] The law of Charles states that the pressure exerted by a gas is proportional to the absolute temperature, provided the volume remains constant.

Having established a close analogy between gases and dilute solutions, as regards the relations between changes of temperature, pressure, and concentration, van't Hoff proceeded to compare the osmotic pressures and gaseous pressures of one and the same substance. He gave a thermodynamical proof of the statement that the osmotic pressure of a gasifiable substance in dilute solution is equal to the pressure of the substance in the state of gas at the same temperature and concentration, provided the law of Henry is supposed to hold good; and he argued that he was justified in substituting osmotic pressure for gaseous pressure in the statement of Avogadro's law, and, therefore, in extending that law to dilute solutions, and asserting that *" Equal volumes of the most different solutions, measured at the same temperature and the same osmotic pressure, contain an equal number of molecules, and that is the number which is contained in an equal volume of a gas at the same temperature and pressure."* [2]

This extension of Avogadro's law was applied by van't Hoff to Pfeffer's experimental measurements of the osmotic pressures of cane-sugar, in aqueous solution, at different temperatures.

"The solution used in Pfeffer's experiments contained one part of sugar in 100 of water; therefore, one gram of sugar was contained in about 100·6 c.c. of the solution. A very striking concordance is noticed, if the osmotic pressures of this solution are compared with the pressures of that volume of a gas, say hydrogen, which contains the same number of molecules, that

---

[1] *Annal. chim. phys.*, (5) **22**, 293 [1881].
[2] *Zeitsch. für physikal. Chemie*, **1**, pp. 490–91 [1887]. " Bei gleichem osmotischen Druck und gleicher Temperatur enthalten gleiche Volume der verschiedensten Lösungen gleiche Molekülzahl und zwar diejenigen, welche bei derselben Spannkraft und Temperatur im selben Volum eines Gases enthalten ist."

is to say $\frac{2}{342}$ gram per 100·6 c.c. ($C_{12}H_{22}O_{11}=342$). As one litre of hydrogen weighs ·08956 gram at 0° and the pressure of one atmosphere, and the concentration we are dealing with is equal to ·0581 gram hydrogen per litre, we have a pressure of ·649 atmosphere at 0°, and ·649$(1 + ·00367t)$ at $t°$. By placing these data beside those obtained by Pfeffer, we have the following results:

Temperature ($t°$).	Osmotic pressure in atmospheres.	·649$(1 + ·00367t)$.
6·8	·664	·665
13·7	·691	·681
14·2	·671	·682
15·5	·684	·686
22	·721	·701
32	·716	·725
36	·746	·735

This relation can be extended, from cane-sugar, to other substances in solution, such as invert-sugar, malic acid, tartaric acid, citric acid, magnesium sulphate and malate, equimolecular solutions whereof were shown by de Vries to exhibit equal osmotic pressures." [1]

Further proofs of the justness of his extension of Avogadro's law were then given by van't Hoff. He showed by thermodynamical reasoning that "*If solutions in the same solvent are isotonic, they must have equal vapour-pressures.*" [2]

Applying this statement to dilute solutions, and accepting the laws already developed by van't Hoff, it follows that equimolecular solutions in the same solvent have equal vapour-pressures; but this statement is nothing else than Raoult's empirical law of the constancy of the molecular depression of the vapour-pressure of a solvent (see p. 155). Proceeding thermodynamically, van't Hoff then shows that "*Solutions in the same solvent, which have the same freezing-point, must be isotonic at that temperature.*" He applies this statement to dilute solutions, accepting the laws already developed, and concludes that solutions which contain the same number of molecules in the same volume, and are therefore isotonic (by Avogadro's law), freeze at the same temperature; but this statement is merely Raoult's experimentally determined law of the constancy of the molecular depression of the freezing-point of a solvent (see p. 151). [3]

---

[1] van't Hoff, *l. c.*, pp. 492–93.

[2] Tammann (*Wied. Ann.*, **34**, 299 [1888]) drew this conclusion from his experimental data.

[3] At this stage of his memoir van't Hoff deduces the expression $K = \dfrac{0·02T^2}{L}$, which has been already referred to and illustrated (see p. 158).

It is evident, van't Hoff said, that if Avogadro's law holds good for dilute solutions, we have a means of determining the molecular weights of dissolved substances, comparable with that whereby the molecular weights of gaseous substances are determined. In the latter cases, molecular weight is deduced from measurements of volume, pressure, and temperature; in the former cases, molecular weight could be deduced from measurements of concentration, osmotic pressure, and temperature. But no accurate and easily used method has yet been found for measuring osmotic pressure; therefore, one of the values which is related to osmotic pressure is measured, namely, depression of freezing-point or increase of boiling-point.[1]

From their very accurate and numerous direct measurements of the osmotic pressures of aqueous solutions of cane-sugar, made in 1905, Morse and Frazer conclude that cane-sugar in aqueous solution exerts an osmotic pressure equal to the pressure which it would exert if it existed as gas, at the same temperature, and with a volume equal to that of the water contained in the solution.[2]

The law of Guldberg and Waage is of fundamental importance in the study of chemical equilibrium. This law states that the rate of chemical action is proportional to the active mass, that is, the molecular concentration, of each substance in the reacting system.[3]

In the ninth section of his memoir, van't Hoff showed that the law of Guldberg and Waage can be deduced, thermodynamically, from the laws which he had established for dilute solutions.

Finally, van't Hoff considered the limits of applicability to dilute solutions of the three laws, namely, the concentrations of dilute solutions are proportional to the osmotic pressures, the absolute temperatures are proportional to the osmotic pressures, and equal volumes measured at equal-temperatures and osmotic pressures contain equal numbers of molecules. He said:

"Dealing with 'ideal solutions,' we are at once confronted with a series of phenomena which are classed by the analogy that has been established between solutions and gases with what used to be called the deviations from Avogadro's law for gases. As the pressure of the vapour of ammonium chloride, for instance, was found to be greater than the pressure calculated on the basis of that law, so is osmotic pressure often found to be abnormally

[1] The development of this part of the subject has been considered (pp. 157–159).
[2] *American Chemical Journal*, **34**, 1 [1905].
[3] This law will be dealt with in the second part of this book (Chapter XIV).

great: and as it was shown, at a later time, that in the first case one had to do with a separation into hydrochloric acid and ammonia, so one is ready to suppose that similar processes happen in certain solutions. It must be granted, however, that the deviations of this kind which occur in solutions are much more numerous, and are exhibited by substances the separation whereof, under ordinary conditions, cannot be accepted without hesitation. For instance, most of the salts, and the strong acids and bases, belong to this class of substances, when in aqueous solution: and this was the reason why what are called the normal molecular depressions of freezing-points and vapour-pressures were not discovered until Raoult made use of organic compounds, for the behaviour of almost every one of these compounds is normal. To give prominence, as I have done, to an Avogadrean law for solutions, appears, therefore, to be a hazardous proceeding; and I should not have done it, had not Arrhenius convinced me, in a letter, that in the cases of salts and similar compounds we have probably to do with separations into ions. So far as investigation has gone, it has been found that solutions which obey the law of Avogadro are non-conductors; and this fact indicates that separation into ions does not occur in these cases: moreover, further experimental proof is found in the fact that the deviations which other solutions show from Avogadro's law can be calculated from their conductivities, by using the assumption which has been made by Arrhenius.

"However this may be, an attempt is made in the sequel to take account of these so-called deviations from Avogadro's law, and to give such a development of the formula of Guldberg and Waage as is made possible by applying the laws of Boyle and Gay-Lussac to solutions."

Proceeding thermodynamically, van't Hoff obtained an expression of the law of Guldberg and Waage which differed from that he had already deduced only in that the new expression contained a certain factor (represented by i) which depended on the molecular concentrations of the solutions. He showed that the experimental data established by Raoult for the depressions of the freezing-points of aqueous solutions enabled values to be found for the factor i, and that the application of the expression, with the values so obtained for the new factor, to many series of measurements of chemical change, gave results which were in close agreement with those established by experiment.

The physical meaning of the factor i, introduced by van't Hoff into the expression of Guldberg and Waage's law, was examined by Planck,[1] who called it "the decomposition-coefficient of the molecules in solution." Planck said:

"If the number of molecules of a dissolved substance is i times greater than would be the case were the normal molecular weight of the substance maintained, then, not one molecule, but i molecules of the substance take part in a chemical reaction, and the number i necessarily enters into the ex-

[1] *Zeitsch. für physikal. Chemie*, **1**, 577 [1887].

pression of Guldberg and Waage's formula, which thereby retains its general signification."

The whole subject of the condition of those homogeneous substances which conduct electricity in aqueous solution was investigated by Arrhenius in memoirs of extreme importance.[1] He supposed that a certain fraction of the molecules of a dissolved electrolyte is separated into ions in a dilute solution, and the ions move independently of one another; such molecules he called *active*, and he applied the term *inactive* to the other molecules, whose ions were supposed by his hypothesis to be firmly bound together. Arrhenius calculated values for van't Hoff's factor i, on the hypothesis that i expressed the ratio between the actual osmotic pressure of a substance in solution and the osmotic pressure which it would exert if it consisted only of inactive molecules. On this basis Arrhenius developed an electrolytic theory of chemical reactions between substances in solution. It would be inconsistent with the plan of this book to consider that theory at present; it will fall into its proper place in the second part of the book, when I am dealing with the history of chemical affinity (Chapter XIV).

The reasoning which van't Hoff used in arriving at the conclusions that the laws of Boyle, Charles, and Avogadro hold good for dilute solutions of homogeneous substances rested on the facts of osmotic pressure, and did not necessarily call in the aid of any hypothesis regarding the origin, or the mechanism of that pressure. It is, however, true that van't Hoff placed the cause of osmotic pressure in the substance in solution, and, for the sake of clearness in thinking, he conceived this pressure to be the result of the movements of the molecules of the dissolved substance. On this view, osmotic pressure must be existent in a solution whether a semi-permeable membrane does or does not separate it from the solvent; the pressure manifests itself when the membrane is placed in position, because the motions of the molecules of the dissolved substance are restrained by the membrane.

In a short paper published in 1890, Lothar Meyer[2] upheld the view that the osmotic pressure of a solution is "the pressure

[1] *Zeitsch. für physikal. Chemie*, **1**, 631 [1887], and other memoirs.
[2] *Zeitsch. für physikal. Chemie*, **5**, 23 [1890].

of the substance which passes through the membrane, not that of the substance for which the membrane is impermeable." He argued that the difference between the pressures of the solvent outside a membrane and the solution inside "depends on the nature of the membrane, and not on that of the liquid "; because, he said, if an aqueous solution of alcohol is separated from pure water by an animal membrane, the water passes into the alcohol and causes the osmotic increase of pressure; but if the same solution is separated from alcohol by a sheet of caoutchouc, an increase of pressure is caused by the flow of the alcohol through the membrane.

The reply of van't Hoff to this criticism was short and convincing.[1] He said that osmotic pressure is a measurable magnitude, capable of thermodynamical treatment; that the analogy between osmotic pressure and gaseous pressure was established by Pfeffer's direct measurements, and can be deduced both from Raoult's work on the depressions of freezing-points and vapour-pressures, and from Henry's law. "Practically, then," van't Hoff said, "the osmotic pressure of a substance in dilute solution is the same as its gaseous pressure." Moreover, van't Hoff argued, if the molecular depression of a solvent (K) is expressed by $\cdot 02\dfrac{T^2}{L}$ (where T = freezing-point and L = heat of fusion of the solvent), then osmotic pressure and gaseous pressure must be equal; now there is ample experimental verification of the statement, $K = \cdot 02\dfrac{T^2}{L}$. To show the justness of his view that osmotic pressure is due to the substance in solution, and not to the solvent, van't Hoff supposes a cell permeable by gaseous hydrogen, but not by nitrogen. Let the cell be filled with nitrogen at the pressure of half an atmosphere, and let it be immersed in hydrogen at the pressure of one atmosphere; as hydrogen can pass freely into and out of the cell, equilibrium will be established between the hydrogen outside and the hydrogen inside the cell, and the pressure due to the hydrogen in the cell will then be one atmosphere; but the total pressure inside the cell will be one and a half atmospheres, and one-third of this (= half an atmosphere)

---

is due to the nitrogen.   Now let the hydrogen be liquefied.   We have a solution of nitrogen in hydrogen, in a cell permeable only by gaseous hydrogen, and the over-pressure (that is, the osmotic pressure) inside the cell is due to the dissolved nitrogen.   If the molecular theory is to be used as an aid towards forming a clear mental picture of the mechanism of osmotic pressure, as the theory has been used as a help towards clear thinking about gaseous pressure, then, van't Hoff said, we must think of osmotic pressure as caused by the movements of the molecules of the substance in solution.   And if the molecular theory should be abandoned, the facts of osmotic pressure will remain, and the analogy which has been established between osmotic and gaseous pressures, by thermodynamical methods, together with the consequences which follow therefrom, will not be overthrown.

An account has been given of Raoult's work on the depressions of the freezing-points of solvents caused by the solution in them of homogeneous substances.   The general result obtained by Raoult was expressed by him in the formula $M = \dfrac{K}{a}$, where M = molecular weight of the substance in solution, a = the depression of freezing-point of the solvent produced by the solution of one gram of substance in 100 grams of solvent, and K is a constant for each solvent, and expresses the depression of the freezing-point thereof which is produced by the solution of one molecular weight of a homogeneous substance in (about) 2 to 15 molecular weights of the solvent.   Raoult obtained two values for K for each solvent he examined.   He explained this result by supposing that the molecules of certain substances are separated by solution completely from one another, while pairs, or it may be triplets of molecules of other substances remain in union and act as single physical molecules (see p. 151). Raoult obtained distinctly anomalous results when he used water as a solvent.   He attempted to make an explanation of these results, by supposing that each physical molecule of water is composed of several chemical molecules (that is, molecules of the composition H_2O), and that salts affect the freezing-point of water as if they were separated by solution in that solvent into their acidic and metallic radicals, and two or more radicals of

the same kind sometimes coalesce to form groups which act as single physical molecules.

Various experimenters established connexions between the depressions of the vapour-pressure of water, produced by the solution therein of homogeneous substances, the weights of the substances in solution, and the temperatures. The measurements made by Raoult proved that the following relation holds good, at any rate for solutions of many organic compounds in solvents other than water: the ratio between the vapour-pressure of the solvent and the depression thereof is equal to the ratio between the sum of the number of molecules of solvent and dissolved substances and the number of molecules of the dissolved substance (see p. 156).

Raoult's results placed the practical aspects of the determination of molecular weights of many homogeneous substances in dilute solutions on fairly satisfactory bases. But investigation was demanded in order to explain many anomalous facts, and to establish precise connexions between the whole series of phenomena, dealt with by Raoult and others, and the established generalizations of chemistry and of physics.

The explanations which were demanded of anomalous results, and the bringing of the new facts within the scope of great general principles, were supplied by the work of van't Hoff, a sketch of which has been given, and that of Arrhenius and other naturalists, which has been referred to in a few words and will be dealt with more fully in a later part of this book. For these investigations showed that homogeneous substances in dilute solutions behave in a way which is strictly analogous with their behaviour as gases; that the generalizations, which express the relations between the volumes, temperatures, and pressures of gases, also express the relations between the concentrations, temperatures, and *osmotic* pressures of dilute solutions; that the deviations from the gaseous laws are reproduced in the deviations from the laws of dilute solutions, and that, as the deviations from the gaseous laws are nothing more than expressions of the limited character of these laws, so the deviations from the laws of dilute solutions are sign-posts which mark the directions to be followed by investigators.

CHAPTER VI.

THE MORE SEARCHING EXAMINATION OF THE COMPOSITION OF HOMOGENEOUS SUBSTANCES. ALLOTROPY.

THE application of the generalization of Avogadro to all substances in the state of gas led to definitions of the terms *atomic weight* and *molecular weight*, and by doing this gave what seemed to be a final answer to the question, What is a chemically homogeneous substance? The molecule of an element was now regarded as a collocation of atoms of one kind, or, in some cases, as identical with the atom; the molecule of a compound was regarded as a collocation of atoms of different kinds. Each chemically homogeneous substance had its own properties which distinguished it from all others; composition and properties were seen to be intimately connected.

But many years before Avogadro's hypothesis was accepted by chemists, facts were known which indicated that identity of properties did not necessarily accompany identity of composition. The accumulation of such facts brought with it the demand for a more searching examination of the expression *identity of composition*.

In 1825, Faraday [1] examined the liquid formed by condensing coal-gas, and obtained from it a compound of carbon and hydrogen, which liquefied at about $0°$ (F.), was composed of 6 parts by weight of carbon combined with one part by weight of hydrogen, and had a specific gravity, in the state of gas, of 27 or 28, referred to hydrogen as unity. Taking the atomic weight of carbon as 6, Faraday expressed the composition of one volume of the vapour of the new compound by the formula C_4H_4 $[(4 \times 6) + (4 \times 1) = 28]$. Another compound of carbon and

---

[1] *Phil. Trans.* for 1825, p. 440.

hydrogen was known, called olefiant gas, the composition of one gaseous volume whereof was expressed by the formula C_2H_2.

Hence the quantities by weight of carbon and hydrogen in one gaseous volume of the new compound were in the same proportion as the quantities of these elements in an equal volume of olefiant gas.

Faraday examined the reaction of the new compound with chlorine, and found it to be different from the reaction between chlorine and olefiant gas:

"This is a remarkable circumstance," said Faraday, "and assists in showing that though the elements are the same, and in the same proportions as in olefiant gas, they are in a very different state of combination."

Faraday remarks that he thinks this is the first time that the existence has been observed of two gaseous compounds "differing from each other in nothing but density." In a note, Faraday refers to observations of others (Serullas, Liebig, and Gay-Lussac), of what seemed to be compounds of the same composition but different properties, and says:

"In reference to the existence of bodies composed of the same elements and in the same proportions, but differing in their qualities, it may be observed, that now we are taught to look for them, they will probably multiply upon us."

In the first German edition of his *Lehrbuch*, published in 1826, Berzelius [1] gave a detailed account of the differences between the properties of oxide of tin prepared by the reaction between tin and nitric acid, and oxide of tin prepared by precipitating perchloride of tin by an alkali, and proved that the two compounds have the same composition.

In 1828, Wöhler [2] obtained urea by heating ammonium cyanate, and showed that the change of properties was not accompanied by any change of composition. Referring to the apparent identity of composition of cyanic acid and fulminic acid,[3] Wöhler said that urea and ammonium cyanate presented

---

[1] *Lehrbuch der Chemie*, vol. ii. p. 271.

[2] *Pogg. Annal.*, **12**, 253.

[3] Wöhler published an investigation of cyanic and fulminic acids in 1822 (*Gilbert's Annal.*, **71**, 95; **73**, 157); Liebig examined the fulminates more fully in 1823–24 (*Annal. Chim. Phys.* [2], **24**, 294; **25**, 285); the investigation was carried further by Wöhler in 1829 (*Pogg. Annal.*, **15**, 622) and ₁by Liebig and

another instance of the possibility of different properties accompanying the same elementary composition.

In 1830, Berzelius proved the identity of composition of tartaric and racemic acids. In his memoir on these acids,[1] Berzelius made some general remarks on substances which have the same composition but unlike properties. He said that such substances ought to receive a class-name; he hesitated between the terms *homo-synthetic* ($\acute{o}\mu o\grave{s}$ = like, and $\sigma\upsilon\nu\theta\epsilon\tau\grave{o}s$ = composed) and *isomeric* ($\acute{\imath}\sigma os$ = equal, and $\mu\acute{\epsilon}\rho os$ = a part), but decided in favour of *isomeric* as shorter and more euphonious. Berzelius then defined isomeric substances as those which have the same chemical composition and the same atomic weight [2] but different properties. He noted the existence of substances having the same composition, different properties, and atomic (molecular) weights which differ by being different multiples of the same value; in 1833 he called these substances *polymeric*.[3]

When two compounds are isomeric, Berzelius proposed to apply the ordinary name to that one formed by an ordinary reaction, and to use the same name with the prefix *para* (in the same sense as in *paradox*) for the other compound; thus he spoke of tartaric acid and paratartaric acid, stannic oxide and parastannic oxide, etc.

In this memoir Berzelius expressed the opinion that when isomerism was more fully investigated, many instances of it would be found.

Is there a similar twofold condition for the elements? asked Berzelius in the same memoir. He recalled the differences between diamond and graphite, and the differences in hardness, solubilities, etc., between platinum obtained by reducing solutions of platinum salts by alcohol, and the same metal obtained by heating the double compound of platinum chloride and ammonium chloride. Berzelius argued that if the

Wöhler in 1830 (*Pogg. Annal.*, **20**, 369). This series of investigations established the identity of composition of the three acids, cyanic, cyanuric, and fulminic.

[1] *Pogg. Annal.*, **19**, 305.

[2] We now say, the same molecular weight.

[3] *Jahresbericht über die Fortschritte der physischen Wissenschaften*, for 1833, pp. 63–67. In these pages Berzelius proposed to apply the term *metameric* (using *meta* in the same sense as in *metamorphosis*) to such isomeric compounds as can be readily changed one into another.

differences between isomeric compounds are connected with differences in the aggregations of their minute particles, then the atoms of an element may probably be arranged in more than one way, and each of these arrangements will exhibit different properties from those of the other arrangements.

In 1831, a note on isomerism was published by Dumas.[1] That naturalist insisted that the parts of the minute particles of homogeneous substances must be arranged in an orderly manner, else constancy of properties would not be observed. He regarded isomerism as conditioned by changes of atomic arrangement. He spoke of "le mouvement moléculaire qui occasione l'isomérie." He thought that degrees of isomerism would be noticed: he regarded changes of density, of hardness, of crystalline form, and the like, as early stages of isomerism; followed, it might be, by changes in chemical properties, without changes of atomic (molecular) weight, and this might lead on to changes of atomic (molecular) weight, without change of elementary composition.

Inasmuch as the values at that time accepted for the atomic weights of platinum and iridium, of cobalt and nickel, of molybdenum and tungsten, of silicon and boron, and of certain other pairs of elements, were either the same or such that one was a whole multiple of the other, Dumas thought that the elements in each of these pairs might be isomeric forms of the same element.

In this note, Dumas spoke of an element existing in its compounds in different forms; for instance, he thought carbon might be electropositive in one part of a certain compound and electronegative in another part of the same compound, and he cited the case of nitrogen, which, he said, is electropositive in the ammonium part of ammonium nitrate and electronegative in the acid radical of the same salt.

A new term was introduced by Berzelius [2] in 1841. He said that the word *isomerism* could not be applied conveniently to the cause of the differences of properties which are sometimes

---

[1] *Lettre de M. Dumas à M. Ampére, sur l'Isomérie* (*Annal. Chim. Phys.*, [2] **47**, 324).

[2] *Jahresbericht* for 1841, part ii, pp. 12–13.

observed in compounds composed of the same numbers of the same atoms. He thought that this phenomenon was due, in some cases at any rate, to differences in the conditions of the elements, or of some of the elements whereof these compounds were formed, and he proposed the term *allotropy* ($\overset{\prime\prime}{\alpha}\lambda\lambda o\varsigma$ = another, and $\tau\rho\acute{o}\pi o\varsigma$ = manner) as a name for the (supposed) different conditions of the same element. Berzelius mentioned carbon, silicon, and sulphur as three elements which exhibited allotropy in a marked manner. At that time (1841) Berzelius regarded isomerism as due sometimes to allotropy, instancing the two forms of sulphide of iron, one of which he thought contained one kind of sulphur and the other contained another kind of sulphur; sometimes to differences in the positions of the atoms, as in methyl acetate and ethyl formate; and sometimes both to allotropy and differences in the positions of the atoms.

Two years later,[1] Berzelius developed his notion of the existence of allotropic forms of the same element in compounds of that element, applying it chiefly to compounds of phosphorus; thus, he thought that ordinary phosphoric acid (formed by the reaction between phosphorus and nitric acid) certainly contained ordinary, or yellow phosphorus, and he spoke of paraphosphoric acid as the acid of red, or amorphous phosphorus.

Finally, I would draw the reader's attention to the statement made by Lucretius, about two thousand years ago, that "it matters much with what others and in what positions the same first-beginnings of things are held in union, and what motions they do mutually impart and receive." [2]

The meanings which are given to-day to the terms *isomerism* and *polymerism* are much the same as the meanings assigned to these words by Ber-

----

[1] *Jahresbericht* for 1843, p. 51.
[2] *De Rerum Natura*, Book II, lines 1007–9 (Munro's translation).

In *The Sceptical Chymist*, published 1678–79, Boyle said: "As the difference of bodies may depend merely upon that of the schemes whereinto their common matter is put, so the seeds of things, the fire and the other agents, are able to alter the minute parts of a body, . . . and the same agents, partly by altering the shape and bigness of the constituent corpuscles of a body, partly by driving away some of them, partly by blending others with them, and partly by some new manner of connecting them, may give the whole portion of matter a new texture of its minute parts, and thereby make it deserve a new and distinct name. So that according as the small parts of matter recede from each other, or work upon each other, or are connected together after this or that determinate manner, a body of this or that denomination is produced, as some other body happens thereby to be altered or destroyed."

zelius. Compounds which have the same molecular weight, and are composed of the same numbers of the same atoms, are called *isomeric*; compounds which may be changed one into another by simple reactions, and are formed by the union of the same relative numbers but different absolute numbers of the same atoms, and have therefore different molecular weights, are called *polymeric*. The word *metameric* is used to-day to denote isomeric compounds which belong to different chemical classes, and exhibit unlike chemical changes under similar conditions. *Allotropy* is now applied to elements only, even more strictly than it was applied by Berzelius; for, whereas Berzelius seems to have thought of allotropic forms of an element as existing in different compounds of that element, the modern usage is to confine the term to the various forms of an element which may have been isolated, and found to differ in specific gravity, hardness, crystalline form, solubility, and other physical properties.

In the article "Isomerism," in the new edition of *Watts Dictionary of Chemistry* (vol. iii., pp. 81, 88 [1892]), Armstrong proposes to use the term "allotropy," as the most general of all the terms applied to the phenomena of identity of composition accompanying differences of properties, and to confine the terms isomerism, metamerism, and polymerism to special kinds of allotropy.[1]

On page 134 I gave a table of vapour-densities and molecular weights from Cannizzaro's memoir published in 1858. That table contains the following data for oxygen and sulphur:

	Molecular weights referred to the weight of a molecule of hydrogen as unity.	Molecular weights referred to the weight of a semi-molecule of hydrogen as unity.
Ordinary oxygen..............	16	32
Electrified oxygen..............	64	128
Sulphur under 1000°...........	96	192
Sulphur above 1000°...........	32	64

The data given by Cannizzaro, and quoted on pages 135, 136, showed that the weight of oxygen contained in a molecule of that element, and in the molecules of various compounds of that element, is always a whole multiple of 16; data were also given by Cannizzaro which showed that the weight of sulphur contained in a molecule of that element, and in the molecules of various compounds thereof, is always a whole multiple of 32: hence, Cannizzaro said, the atomic weights of oxygen and sulphur are 16 and 32, respectively.

---

[1] The meanings given at different times to the words *isomerism, metamerism* and *polymerism* are arranged in tabular form in Miss Freund's *The Study of Chemical Composition*, p. 570. [1904].

Cannizzaro also concluded that the molecule of ordinary oxygen is composed of 2 atoms of oxygen, and the molecule of electrified oxygen of 8 atoms of the same element, and he represented these molecules by the symbols O_2 and O_8, respectively. Similarly, he represented the molecule of sulphur-gas under 1000° by the symbol S_6, and the molecule of the same element, in the state of gas over 1000°, by the symbol S_2.

More accurate experiments than those whose results were used by Cannizzaro have shown that the molecular weight of electrified oxygen, or ozone, is 48; hence the symbol of this modification of oxygen is O_3.

Ozone is an allotropic form of oxygen. The differences, which are considerable, between these substances are connected with differences in the numbers of atoms which constitute their molecules. This example shows that a collocation of two atoms of the same kind has properties which differ from those of a collocation of three of the same atoms.

Although the properties of sulphur-gas below 1000° have not been compared in detail with the properties of sulphur-gas considerably above 1000°, there can be no doubt that the group of six atoms which is the molecule of this element at the lower temperature has different properties from those of the group of two atoms which is the molecule of the same element at the higher temperature.

A short description was given in Chapter V of the development of methods for determining the molecular weights of homogeneous substances in dilute solutions. The application of these methods to sulphur has shown that the molecules of this element which are present in a dilute solution of it in carbon disulphide, and in napthalene, are probably composed of eight atoms, whereas the molecules of the same element in a dilute solution of sulphur in benzene are probably composed of six atoms.[1]

Similar results have been obtained for certain other elements; for instance, a dilute solution of iodine in ether probably con-

---

[1] See, for instance, Paterno and Nasini, *Berichte*, **21**, 2153 [1887]; Beckmann, *Zeitsch. für physikal. Chemie*, **5**, 76 [1889]; Herz, *l. c.*, **6**, 358 [1890]; Helff, *l. c.*, **12**, 196 [1893].

tains molecules each composed of four atoms, and a dilute solution of the same element in carbon disulphide probably contains some molecules composed of three atoms and some composed of two atoms of iodine.[1]

With the exception of the case of oxygen and ozone, the most marked differences between the properties of the same element are shown by carbon, boron, and silicon. As the molecular weights of these elements have not been determined, for none has been gasified, or dissolved without chemical change, it is impossible to say whether the molecular weight of one form is different from those of the other forms. In these cases, allotropy may accompany differences in the numbers of atoms which form the molecule of the element under different conditions; but if the molecular weights of the various modifications of each of these solid elements should be determined by methods yet to be discovered, and should be found to be the same, then we shall be obliged to say that these cases of allotropy are examples of isomerism, and to connect the differences between the properties of the various forms of each element with differences in the arrangements of the same number of the same atoms.

Equal weights of the different allotropic forms of an element contain different quantities of energy. (See Chapter XVI.)

Every year, every month indeed, adds to the number of isomeric compounds, that is, compounds whose percentage compositions and molecular weights are the same while their reactions are different. As the molecules of all the members of a series of isomeric compounds are composed of the same number of the same atoms, the only way in which the differences between the reactions of these compounds can be expressed at present is by saying that the arrangement of the atoms in any one molecule is not the same as the arrangement of the atoms in any other isomeric molecule. There are also differences between the energy-contents of isomeric compounds and between the energy-contents of allotropic forms of the same element. In his *Principles of Inorganic Chemistry*, p. 80 (1st ed.), Ostwald says:

---

[1] See, for instance, Loeb, *C. S. Journal*, **53**, 805 [1888].

"Elements which, by reason of different energy-content, have different properties, are allotropic." (See Chapter XVI.)

I shall endeavour, in another chapter, to trace the history of the hypotheses and conventions which have led to a working method of expressing the differences between the arrangements of atoms, and connecting these with the reactions and properties of isomeric compounds.

In 1819, Mitscherlich proved that identity of composition is sometimes accompanied by difference of crystalline form, and identity of crystalline form (as such identity was then understood) may be associated with difference of composition. Between 1820 and 1840, Faraday, Liebig, Wöhler, Berzelius, and other investigators proved that several homogeneous substances may have the same composition and the same relative density as gases, and yet differ in physical properties and in chemical reactions, and that the properties of an element may vary according to the method whereby it is obtained from its compounds, or the conditions to which it is subjected. Cannizzaro and others applied the generalization of Avogadro to the facts of composition and properties, and since 1860 it has been necessary to define identity of composition in terms of the theory of atoms and molecules, and to say that it consists in identity of nature, number, and arrangement of the atoms which form the molecules of homogeneous substances.

CHAPTER VII.

ELEMENTS WHICH DO NOT REACT. ARGON AND ITS COMPANIONS.

UNTIL the year 1894, chemists thought of elements as homogeneous substances which are changed by combining with other homogeneous substances, and, in some cases, also exhibit changes of physical properties, or of readiness to participate in chemical reactions without the addition to them of other substances. But at the Oxford meeting of the British Association in 1894, Lord Rayleigh and Professor Ramsay announced the isolation of a new element which refused to react with other substances under any conditions to which it had been subjected.

A full account of the isolation of the new element, and a description of some of its properties were given by Rayleigh and Ramsay in 1895.[1] The year before, Lord Rayleigh had published [2] data which showed that nitrogen obtained from the atmosphere is about one-half per cent. heavier than nitrogen prepared from nitrous oxide, nitric oxide, or ammonium nitrite.

Rayleigh and Ramsay proved that the comparative lightness of "chemical nitrogen" (that is, nitrogen prepared from a compound of that element) was not due to the presence in it of any substance known to chemists, and almost certainly was not due to the separation of some of the molecules of nitrogen into atoms. They then said:

"Regarding it as established that one or other of the gases [nitrogen from the atmosphere, or nitrogen from a compound thereof] must be a mixture, containing, as the case might be, an ingredient much heavier or much lighter than ordinary nitrogen, we had to consider the relative probabilities of the various possible interpretations. Except upon the already discredited hypothesis of dissociation, it was difficult to see how the gas

---

[1] *Phil. Trans.*, **186**, 187 [1895].   [2] *Proc. R. S.*, **55**, 340 [1894].

of chemical origin could be a mixture. To suppose this would be to admit two kinds of nitric acid, hardly reconcileable with the work of Stas and others upon the atomic weight of that substance. The simplest explanation in many respects was to admit the existence of a second ingredient in air from which oxygen, moisture, and carbonic anhydride had already been removed. The proportional amount required was not great. If the density of the supposed gas were double that of nitrogen, one-half per cent. only by volume would be needed; or, if the density were but half as much again as that of nitrogen, then one per cent. would still suffice. But in accepting this explanation, even provisionally, we had to face the improbability that a gas surrounding us on all sides, and present in enormous quantities, could have remained so long unsuspected."

Rayleigh and Ramsay proposed to examine "the evidence in favour of the prevalent doctrine that the inert residue from air after withdrawal of oxygen, water, and carbonic anhydride is all of one kind."

In a memoir published in 1785,[1] Cavendish expressed doubt as to the homogeneity of what was then called *phlogisticated air* (in modern nomenclature, nitrogen). He said:

"I therefore made an experiment to determine whether the whole of a given portion of the phlogisticated air of the atmosphere could be reduced to nitrous acid [we would now say, oxidized to nitric acid], or whether there was not a part of a different nature to the rest which would refuse to undergo that change. . . . For this purpose I diminished a similar mixture of dephlogisticated air and common air, in the same manner as before,[2] till it was reduced to a small part of its original bulk. I then, in order to decompound as much as I could of the phlogisticated air [nitrogen] which remained in the tube, added some dephlogisticated air [oxygen] to it and continued the spark until no further diminution took place. Having by these means condensed as much as I could of the phlogisticated air, I let up some solution of liver of sulphur to absorb the dephlogisticated air; after which only a small bubble of air remained unabsorbed, which certainly was not more than $\frac{1}{120}$ of the bulk of the phlogisticated air let up into the tube; so that, if there is any part of the phlogisticated air of our atmosphere which differs from the rest and cannot be reduced to nitrous acid, we may safely conclude that it is not more than $\frac{1}{120}$ part of the whole."

Cavendish did not examine the small quantity of gas which was not "reduced to nitrous acid"; his experiment left undecided the question whether "the inert residue from air, after

---

[1] *Phil. Trans.*, **75**, 372 [1785].
[2] Cavendish had passed electric sparks through a mixture of common air and dephlogisticated air (oxygen), standing over a solution of caustic soda, and had found that nitric acid was produced.

withdrawal of oxygen, water, and carbonic anhydride, is all of one kind."

After describing Cavendish's experiment, Rayleigh and Ramsay proceed:

"The concord between the determinations of density of nitrogen obtained from sources other than the atmosphere, having made it at least probable that some heavier gas exists in the atmosphere hitherto undetected, it became necessary to submit atmospheric nitrogen to examination, with a view of isolating, if possible, the unknown and overlooked constituent, or, it might be, constituents."

Three methods were used with the object of separating the substance, or substances supposed to be present in "atmospheric nitrogen." Nitrogen from the air was sparked with oxygen in presence of alkali, atmospheric nitrogen was absorbed by hot magnesium, and air was submitted to a prolonged process of diffusion.

When nitrogen which had been separated from the atmosphere was mixed with oxygen, and electric sparks were passed through the mixture standing over an aqueous solution of potash, a gas always remained unabsorbed by the alkali, and the quantity of this gas "was in proportion to the amount of air operated upon." A comparison of the spectrum of air with that of the residual gas showed that the gas did not consist of nitrogen only.

Nitrogen prepared from the atmosphere was passed through substances which freed it from water, carbonic anhydride, and other possible impurities, and then over hot magnesium as long as gas was absorbed, and the gas which remained was kept in contact with fresh quantities of hot magnesium. About 50 c.c. of a gas were thus obtained, which weighed about 2·7 mgm. more than an equal volume of nitrogen obtained from ammonium nitrite. This process was repeated on a much larger scale, and about 200 c.c. were obtained of a gas which was 16·1 times heavier than hydrogen. The gas which was not absorbed by hot magnesium was mixed with oxygen; the mixture was sparked over alkali; and the residual gas was found to have the specific gravity 19·086, and to exhibit many spectral lines which differed from those belonging to any known substance

Air was passed slowly through a series of tobacco-pipes, enclosed in a glass tube wherein a partial vacuum was maintained, and about 2 per cent. of the air which entered the pipes was collected at the other end by means of a water-aspirator; oxygen, water, carbonic anhydride, and ammonia were removed from the air which collected in the aspirator, and a gas was thus obtained which was about 2 per cent. heavier than "chemical nitrogen." This result confirmed the supposition that "atmosperic nitrogen" is a mixture of nitrogen and a heavier gas.

Large volumes of nitrogen prepared from ammonium nitrite (in one case about 5 litres, in another case about 15 litres) were mixed with oxygen, and sparked over alkali: a few c.c. remained (in one case, 3 c.c.; in the other, 3½ c.c.) of a gas which showed the same spectrum as the gas obtained from atmospheric nitrogen. It was shown afterwards that those minute quantities of the gas which was not nitrogen came from the water used in the experiments, and from air which leaked into the apparatus during the experiments.

The results of these experiments established the facts that "nitrogen" obtained from the atmosphere contains a gas considerably heavier than pure nitrogen, that this gas is slightly soluble in cold water, and that nitrogen prepared from ammonium nitrite (and other compounds of nitrogen) does not contain this gas. The new constituent of the atmosphere was then prepared in quantity by causing atmospheric nitrogen to pass to and fro over layers of hot magnesium, in an apparatus which worked automatically, with all the precautions which the preliminary experiments had shown to be necessary; the water required in this experiment was saturated with the new gas before it was used. The new gas was also prepared in quantity by sparking atmospheric nitrogen with oxygen over alkali, in a modified form of apparatus, which worked at a rate about 3000 times greater than that of the apparatus used by Cavendish.

The density of the new gas obtained by the magnesium-method was found to be 19·9, and the density of the gas obtained by sparking to be 19·7. The gas exhibited two distinct and very characteristic spectra which were different from those of any

other "spectrum-giving gas or vapour." [1]   About 4 c.c. of the new gas were found to dissolve in 100 c.c. of cold water.

Determinations of the specific heats of the new gas at constant volume and constant pressure proved the ratio between these constants to be 1·644:1; as 1·66:1 is the theoretical ratio for a monatomic gas, that is, "a gas in which all energy imparted to it at constant volume is expended in effecting translational motion," the conclusion followed that the new gas is monatomic, or, in other words, that its molecular and atomic weights are identical.   Hence the gas must be either an element or a mixture of elements.

A long series of attempts was made to cause the new gas to combine with elements and compounds; all the results were negative.   Hence the name given by its discoverers to this gas, *argon* (from $\overset{\prime\prime}{\epsilon}\rho\gamma o\nu$ = work, and α in the sense of negation).   As argon is 19·9 times heavier than hydrogen, and is a monatomic gas, the atomic weight of argon is (approximately) 39·8, and its molecular weight is expressed by the same number.   Later determinations gave the value 39·9.

Regarding the question as to the homogeneity of argon, Rayleigh and Ramsay said:

"There is evidence both for and against the hypothesis that argon is a mixture: for, owing to Mr. Crookes's observation of the dual character of its spectrum; against, because of Professor Olszewski's statement that it has a definite melting-point, a definite boiling-point, and a definite critical temperature and pressure; [2] and because, on compressing the gas in presence of its liquid, pressure remains sensibly constant until all gas has condensed to liquid.   The latter experiments are the well-known criteria of a pure substance; the former is not known with certainty to be characteristic of a mixture."

Many papers have been published on argon, by Ramsay and by others, since 1895, wherein the physical properties of this substance are described, and its occurrence in various spring-waters and minerals notified.   No one has succeeded in causing argon to react with other substances.   All the attempts which

---

[1] For details of spectra, see Crookes, *Phil. Trans.*, **186**, 243 [1895].
[2] For details, see Olszewski, *Phil. Trans.*, **186**, 253 [1895].   Boiling-point, −187°; melting-point, −189·6°; critical temperature, −121°; critical pressure, 50·6 atmospheres.

have been made to separate it into two or more distinct substances have failed.[1]

The question whether argon is one element or a mixture of elements cannot yet be regarded as finally decided. Attention was drawn recently to the insufficiency of any purely physical evidence to decide this question by Martin,[2] who argued that the characteristic of every element is the power of producing "its own peculiar set of compounds."

"Were *argon* a *mixture* of three monatomic gases of like nature, and of which the atomic weights differed from each other by a fraction of a unit—as do those of nickel and cobalt—it would be impossible to distinguish the mixture from an element. . . . It takes many thousands of fractionations to distinguish between two rare earths which not only give different chemical compounds, but are far more unlike chemically than would be three *monatomic inert gases*."

In the spring of 1895, Ramsay announced the isolation of a new gas from a mineral named clèveite (a uranate of lead containing rare earths).[3] The spectrum of the new gas showed a bright yellow line identical in wave-length with the solar line D_3, which was discovered by Lockyer in 1868, and thought to be caused by a hypothetical substance, unknown on the earth, to which the name *helium* was given. Because of this identity, Ramsay named the new gas *helium*.

In 1898, Ramsay published an account of his experiments on the fractionation of liquefied argon obtained from the atmosphere, and announced the separation of four new gases, to which he gave the names *neon* (νέος = young, or new), *krypton* (κρυπτός = hidden), *xenon* (ξένος = stranger), and *metargon*.[4] Investigations made at a later time showed that the spectrum which was thought to be characteristic of metargon was really due to some compound of carbon.[5] The claim of the other three gases to be recognized as distinct homogeneous substances has been confirmed by searching investigations.[6]

---

[1] See especially Ramsay and Collie, *Proc. R. S.*, **60**, 206 [1896–97]; and Ramsay and Travers, *Phil. Trans.*, **197**, 47 [1901].

[2] *Proc. C. S.*, **17**, 259 [December 31, 1901].

[3] *Proc. R. S.*, **58**, 65, 81. A fuller account is given in *C. S. Journal*, **67**, 684 [1895].

[4] *Proc. R. S.*, **63**, 437 [1898]; *Berichte*, **31**, 3111 [1899]; *Proc. R. S.*, **67**, 329 [1901].

[5] *Proc. R. S.*, **67**, 329 [1901].

[6] See e.g. *Proc. R. S.*, **60**, 206 [1896–97]; and, more especially, *Argon and its Companions*, by Ramsay and Travers, *Phil. Trans.*, **197**, 47 [1901].

The ratio of the specific heats shows that helium, neon, krypton, and xenon are monatomic gases. None of them has been separated into unlike portions by any physical process, nor has any been caused to take part in a chemical change. Each has its characteristic specific gravity, critical pressure and temperature, refractivity, and spectrum.[1]

The spectral lines characteristic of helium have been found in specimens of neon, and the specially characteristic helium line D_3 has been noticed in the spectrum of the atmosphere;[2] hence all the inactive elements, argon, helium, neon, krypton, and xenon, exist in the atmosphere.[3]

I have now indicated the chief lines of movement which have marked the examination of the composition of substances from early times to the present day.

A definite theory, to the effect that matter has a grained structure, was announced by the Greek thinkers 500 years before Christ. According to that theory, the grains are unchangeable in number and properties, and all material changes consist in rearrangements of these grains. This theory implied the theoretical definition of a homogeneous substance as a substance composed of grains all of one kind.

From the early years of the Christian era until towards the middle of the eighteenth century, no general theory can be discovered of what we now call the composition of substances. Vague notions prevailed concerning Principles, and Elements, common to many substances; these Principles and Elements were thought of as class-properties of substances, and yet capable of being removed without destroying the essential natures of the substances. The notion of an intimate and necessary union between properties and composition had disappeared; or, per-

---

[1] Helium has not been liquefied; the boiling- and melting-points of neon have not yet been determined accurately [April, 1906].

[2] Baly, *Nature*, October, 1898; Kayser, *Chem. News*, August 23, 1895; Friedländer, *Chem. News*, Dec. 9, 1895.

[3] A popular account of "The Inert Gases of the Atmosphere," by Prof. Ramsay, will be found in the *Popular Science Monthly* for October, 1901. Ramsay's book, *The Gases of the Atmosphere, the History of their Discovery* [Macmillan, 1896], contains an account of the examination of the composition of the air. A list of memoirs on helium is given at the end of a paper, " l'Helium," by Ramsay, in *Annal. Chim. Phys.* (7), **13**, April, 1898.

haps it would be more correct to say that the meanings given to such terms as *properties* and *composition* were so vague, changeable, and unlike the meanings we give to these terms to-day that we cannot translate into modern phraseology the language wherein the alchemists sought to express their answers to the question, What is a homogeneous substance?

All substances were regarded by the alchemists as manifestations of the *One Essence*, hidden by the wrappings of specific properties. To remove the properties, and manipulate the life, soul, or essence of things was the aim of alchemy.

Before the close of the alchemical period we find several exact students of nature who had gained fairly clear conceptions of composition; the most notable of these was Boyle.

The preparation had been long and varied: suddenly, it seems to us as we look back, chemistry began, fashioned, from the materials which the centuries had gathered, by a man of supreme genius. Lavoisier was dowered by nature with the power of thinking accurately, and, as we say, scientifically. He did not free himself from the trammels of the alchemists and the phlogisteans; he was free-born.

After Lavoisier, the notion of the element and the compound became more full of meaning. Dalton applied the atomic theory of the Greeks to the facts which had been amassed by others concerning the compositions of compounds. And after Dalton had given chemistry that general conception which has been its guide ever since, Berzelius broadened and strengthened the experimental foundations of the Daltonian theory. By introducing the notion of the molecule, Avogadro extended the range of the theory of the grained structure of matter. Since 1811 it has been possible to give quantitative definitions of the terms *element* and *compound*. Rayleigh and Ramsay have extended the conception of the chemical element by proving the existence of homogeneous substances which refuse to participate in interactions with other substances.

The beginning of the new century has brought new views of the constitution of matter. The formation of a compound seems to be the same in kind as the formation of an element. What we have thought of as the simplest thing—the atom—is proving

itself to be a vastly complicated structure. Nevertheless the Lavoisierian description of the element, and the atomic and molecular theory of material structure, remain as finger-posts which point the ways that must be followed.[1]

---

[1] The descriptions which have been given recently of elements and compounds in the language of the phase-rule will be referred to in Chapter XVI. The electronic theory, which will be referred to in Chapter XII, provides for the existence of non-active elements.

APPENDIX TO PART I.

CHEMICAL NOMENCLATURE AND NOTATION.

To write a full description of the origin, growth, and misadventures of the language of chemistry is to write a history of the science. I shall merely note a few points of fundamental importance in the lines of advance of chemical nomenclature and notation.

In his memoir on chemical nomenclature, referred to on the next page, Lavoisier said:

"Every physical science is formed, necessarily, of three things: the series of facts which constitute the science, the ideas which recall, and the words which express, these facts. The word ought to call forth the idea, the idea depict the fact: they are three impressions of the same seal." [1]

The knowledge of the transformations of matter possessed by the alchemists was vague and flaccid; hence their language was hazy and inaccurate: moreover, many of them used expressions which were meant to mislead the ordinary reader. Almost the only thing that can be affirmed with certainty regarding the *mercury, salt, sulphur,* and *water* of the alchemists is, that these terms had not the meanings which ordinary people gave them. Alchemical language was based on far-fetched, fanciful analogies; in that language the word did not call forth any just and clear idea, the idea did not depict any definite fact. The fanciful language of alchemy was followed by terms which, like those they superseded, were based on vague and superficial analogies. Lavoisier found it impossible to describe

---

[1] *Toute Science physique est necessairement formée de trois choses: la serie des faits qui constituent la science, les idées qui les rapellent, les mots qui les expriment. Le mot doit faire naître l'idée, l'idée peindre le fait: ce sont trois empreintes d'un même cachet.*

the facts which he observed in a language that spoke of *flowers of zinc, diaphoretic antimony, butter of antimony, powder of algaroth, red precipitate, vitriolated tartar, spirit of sulphur,* and *ethiops per se.* Such a language was not what Lavoisier said a language ought to be; it was not "an analytical method whereby we proceed from the known to the unknown." [1]

The true principles of chemical nomenclature were stated and illustrated in three memoirs contributed to the French Academy of Science in 1787 by Lavoisier, de Morveau (afterwards de Guyton), and de Fourcroy.[2] Lavoisier's memoir lays down the principles of chemical nomenclature; the memoir of de Morveau illustrates these principles, and applies them in detail; de Fourcroy gives a tabular arrangement of the names of the most important members of the various classes of chemical substances. The *Méthode de Nomenclature chimique* also contains two lists of the older names, and the new names proposed, of about seven hundred substances.

The new nomenclature gave a distinctive name to every simple substance, "recognizing as simple all the substances which we have not been able to decompose." The well-established names of simple substances were retained; but if the common name evidently conveyed a false idea, or led to confusion, a new name was substituted, "generally taken from the Greek," which sought to express the most characteristic and important property of the substance.[3] The names proposed for the compounds of two simple substances were based on the

---

[1] "Les langues . . . sont . . . de véritables méthodes analytiques à l'aide desquelles nous procédons du connu à l'inconu." Lavoisier, 1782. (For reference see next note.)

[2] (1) *Mémoire sur la nécessité de reformer et de perfectionner la Nomenclature de la Chimie* (Lavoisier). (2) *Mémoire sur la développement des principes de la Nomenclature méthodique* (de Morveau). (3) *Mémoire pour servir à l'explication du Tableau de Nomenclature* (de Fourcroy). The three memoirs were published (in 1787) in a book entitled *Méthode de Nomenclature chimique proposée par MM. de Morveau, Lavoisier, Bertholet, et de Fourcroy.* An English translation of de Fourcroy's table, by George Pearson, somewhat altered and considerably enlarged, was published in 1799 with the title, *A Translation of the Table of Chemical Nomenclature Proposed by de Guyton, formerly de Morveau, Lavoisier, Bertholet, and de Fourcroy; with explanations, additions, and alterations. To which are subjoined Tables of single elective attractions, Tables of chemical symbols, Tables of the precise forces of chemical attraction, and Schemes and explanations of cases of single and double elective attractions.*

[3] An interesting memoir on the etymological history of the names of the elements, by P. Diegart, will be found in *J. prakt. Chem.* (Neue Folge), Bd. **61**, p. 497 [1900].

classification of these compounds; to each was given a class-name which recalled the properties common to many individuals, and a specific name which expressed a particular property of the individual compound. The notion of *properties* was used to include that of *composition*.

The "simple combustible substances" (except hydrogen), and the hypothetical radicals of acids, were classed together under the name "*acidifiable bases*." Only four simple acidifiable bases were known in 1787, namely, carbon, nitrogen, phosphorus, and sulphur. The class of *acidifiable bases* contained such names as "*radical tartarique*," "*radical muriatique*," and the like; acids were supposed to be formed by the union of these "*acidifiable principles*" (including in this term the four elements, carbon, nitrogen, phosphorus, and sulphur) with "*the acidifying principle*," that is, oxygen; *acide muriatique*, for instance, was regarded as a compound of oxygen with the *radical muriatique*. When two acids were known composed of the same acidifiable base and oxygen, they were distinguished by using an adjectival form of the name of the base and changing the termination thereof; thus, one had *l'acide sulfureux* and *l'acide sulphurique*.

The binary compounds of oxygen which are not acids were named *oxides*, and distinguished as *oxide of iron, oxide of bismuth*, etc.

In naming compounds of these simple substances, and especially salts, the French chemists said that regard should be paid to (1) the relative quantity of the acidifying principle common to all members of a class, (2) the acidifiable principle from which the proper acid of the class is produced, and the relative quantity of this principle, and (3) the saline, earthy, or metallic base which determines the particular member of the class. The name given to each class of salts was derived from that of the common acidifiable principle, and each salt was distinguished by the name of the base peculiar to it. Variations in the terminations of the names of the acids indicated the proportion between the quantities of the acidifying and the acidifiable principles (in modern language the proportion between oxygen and the non-metal); and the use of the qualifying terms *acidu-*

lated and *basic* indicated whether there was more than sufficient acid to saturate the base, or more than sufficient base to saturate the acid.

In the following examples the English equivalents of the names proposed by the French chemists for certain salts are contrasted with the older names.

Sulphate of potash—formerly called *Vitriolated tartar.*

Acidulated   sul-
  phate of potash
	"	"	*Vitriolated tartar with ex-*
			  cess of acid.

Sulphate of soda	"	"	*Glauber's salt.*
Sulphate of iron	"	"	*Vitriol of iron.*
Sulphite of potash	"	"	*Stahl's sulphuretted salt.*
Nitrate of potash	"	"	*Common nitre.*
Nitrate of soda	"	"	*Cubic nitre.*

The naming of organic compounds which are not acids or salts was necessarily less developed than that of the inorganic compounds which had been more thoroughly studied and classified. The name *alcohol* [1] was given to many compounds obtained by purifying various natural oils and similar substances by distillation; the products of the reactions between alcohols and acids were called *ethers.* Individual alcohols were distinguished by such names as *alcohol of guiacum, alcohol of myrrh, alcohol of wine,* and the like; ethers were distinguished as *sulphuric ether, muriatic ether, acetic ether,* etc. Other class-names of organic compounds were *fixed oils, sugars, gums, resins,* and the like.

Changes have been made in the application of the principles of chemical nomenclature which were enunciated by Lavoisier and his associates, and the development of the science has necessitated a vast enlargement of the language. Acids are not now regarded as compounds of oxygen with simple or compound radicals, and many other changes have been made in the conceptions of the connexions between composition and reactions which prevailed towards the end of the eighteenth century.

---

[1] " To *alkoolize,* is to reduce solid substances into a very fine impalpable powder; and it is likewise to purify and refine all spirits and essences of their Flegm, and other impurities; whence the Spirit of Wine well rectified, is called the *alkool* of Wine." *The Compleat Chymist,* by Christopher Glaser [1677].

The molecular and atomic theory has completely altered that part of the science which deals with organic compounds. Nevertheless, it is true that the principles which were laid down and applied by the French chemists in 1787 are the foundation of the chemical language of to-day.[1]

It has been customary in chemistry for many centuries to express the names of substances, and the prevalent views regarding their mutual relations, by signs as well as by words. The alchemists regarded gold as the perfect metal, and they used the circle to express this conception; they thought of silver as a semi-perfect metal, and their sign for silver was a half-circle. Certain metals were placed by them in the gold class, others in the silver class, others in both these classes; as these metals were all thought to be imperfect, their symbols were constructed by joining the circle, the half-circle, or both, with signs which denoted imperfection. The signs most commonly used to express imperfection were the cross and the dart. The following symbols for metals illustrate the alchemical notation:

Gold, the perfect metal, ◯. Silver, the semi-perfect metal, ☽.

Copper ♀ ⎫
Iron ♂ ⎬ imperfect metals of the gold-class.
Antimony ♁ ⎭

Tin ♃ ⎫
Lead ♄ ⎬ imperfect metals of the silver-class.

Mercury ☿ an imperfect metal, belonging to both the gold and the silver-class.

Various class-symbols were employed by the alchemists, and also by the earlier chemists. In Bergman's notation, for instance (seventies and eighties of the eighteenth century), the sign ♚ denoted a metallic substance, salts were represented by the sign ◯, alkalis by ⊖, acids by +, and calces by the sign ♅. Special signs were used for the individual substances in each class; thus + ⊕ signified sulphuric acid, and ♅ ◓ the calx of zinc.

---

[1] The nomenclature, especially of organic compounds, adopted by the Chemical Society is described in *C. S. Journal*, **35**, 276 [1879] and **41**, 247 [1882].

On pages 66 to 68 I gave an example of the use which Lavoisier made of signs in 1782, to express the quantities and the arrangement of the substances in a system before and after chemical change.

In 1787 two memoirs were published by Hassenfratz and Adet, wherein a fairly complete system of chemical symbols was described.[1] The objects which these writers set before themselves were to assign a symbol to each known simple substance, and to construct such symbols for compounds as should indicate the nature, and number, and the relative quantities of their simple components. Hassenfratz and Adet used straight lines and semicircles as symbols for the non-metallic simple substances ("*the simple acidifiable bases* "), and circles enclosing the initial letters of their names as symbols for the metals. The radicals of acids ("*the acidifiable compound bases* ") were denoted by squares, enclosing the initial letters of the names of the radicals. The sign △ denoted an alkali; potash was expressed by △̲ᴘ, soda by △̲ₛ. The sign ▽ denoted a fixed earth; chalk was expressed by ▽̄ᴄ, alumina by ▽̄ᴀ.

The symbols for compounds were formed by putting together the symbols of their constituents. Thus, sulphide of nickel was represented by the symbol ⦶ᴺ, formed of ⊚ the symbol for nickel, and ⌣ that for sulphur; phosphide of lead was symbolized thus ⦵ᴘ, formed from the symbol for lead (*plumbum*) and ⌢ the symbol for phosphorus. A vertical straight line attached to a symbol indicated the substance to be a gas; thus, from the symbols ⌣ and), standing for sulphur and hydrogen, there was formed the symbol ⌇ for gaseous sulphuretted hydrogen. The sign ∨ was used to indicate a liquid substance. The symbols of the five oxides of nitrogen were constructed by combining the symbol / for nitrogen, with — the symbol for oxygen: three gaseous oxides were sym-

---

[1] *Mémoires sur de nouveaux Caractères à employer en Chimie.* The two memoirs are appended to the edition which I have consulted of *Méthode de Nomenclature chimique proposée par MM. de Morveau, Lavoisier, Bertholet, et de Fourcroy* (see foot-note, p. 190).

bolized, ⌒ , ⌒ , and ⊢; and two liquid oxides were repre-
sented by these symbols, ∨⊢ and ∨∠. Three compounds of
sulphur and potash are mentioned by Hassenfratz and Adet;
one neutral, one with excess of sulphur, and one with excess of
pctash: in the symbols given to these compounds, the relative
quantities of the constituents were indicated by changing the
position of the symbol for sulphur; the symbols were:

Neutral.   Excess of sulphur.   Excess of potash.

Hassenfratz and Adet gave symbols for fifty-four "simple"
substances, including the "acidifiable compound bases"; by
placing the symbols in different positions, expressions could be
formed for the composition of 322,452 compounds, each con-
sisting of three "simple" substances.

In their report to the French Academy on this system of
notation, Lavoisier, Berthollet, and de Fourcroy said they
thought the symbols had the great merits of bringing facts, and
not merely words, before the eye, giving just ideas concerning
the compounds represented, and fixing the symbols of compounds
to be discovered, in accordance with a definite rule.[1]

In his *New System of Chemical Philosophy* Part I (published
in 1808), Dalton represented the compositions of compounds by
placing together the symbols which he used for the elements;
he repeated the symbol of an element as many times as there
were atoms of that element in an atom of the compound. He
used circles with lines and dots as symbols for the six non-
metallic elements known to him at that time (carbon, hydrogen,
nitrogen, oxygen, phosphorus, and sulphur); and circles en-
closing the first letters of the English names of the metals as
symbols for that class of elements. Dalton's symbols for
nitrogen, hydrogen, and oxygen, respectively, were ⊕ , ⊙ ,
and ○. He supposed ammonia to be a compound of one atom
of hydrogen and one of nitrogen, and therefore represented it

---

[1] Two interesting papers on the symbols used by pharmacists in the seventeenth
century, by Dr. G. B. Plowright, appeared in *The Pharmaceutical Journal* for
February 25th and May 20th, 1905. A third paper appeared on May 19, 1906.

by the symbol ⦿ ; he used the symbol ⦿◯ for nitric acid, because he thought that nitric acid was formed by the union of one atom of nitrogen with two atoms of oxygen; as he regarded water to be a compound of one atom of hydrogen and one atom of oxygen, he gave it the symbol ◯◯ . From the facts then known about the composition of ammonium nitrate Dalton concluded that compound to be formed of one atom of ammonia, one atom of nitric acid, and one atom of water, and

he expressed that composition by the symbol .

About 1814, Berzelius introduced the system of notation which is now used with certain modifications and additions.[1] Berzelius used the first letter, or the first and second letter, or the first letter and the first consonant, of what he called the Latin name of an element, as the symbol for that element.[2] His system of expressing the compositions of compounds was based, like that of Dalton, on the atomic theory.   He expressed the number of atoms of an element in a compound atom by placing an Arabic numeral before the symbol of the element; and he interposed the sign of addition between the symbols of the elements: thus, to copper oxide he gave the symbol $Cu + O$, and to sulphur trioxide the symbol $S + 3O$.   When two similar compounds combined, say, two oxides, Berzelius placed the sign of addition between the symbols of the compounds, and expressed the number of atoms of each element, when that number was greater than one, by a small Arabic numeral placed above the symbol of the element: thus, to copper sulphate he gave the symbol $CuO + SO^3$; to nitrate of potassium,[3] the symbol $2NO^6 + PoO^2$; and to sulphate of potassium,[3] the symbol $2SO^3 + PoO^2$.   At a later time (for instance, in the German edition of his *Lehrbuch* published in 1827), Berzelius represented the number of atoms of oxygen in a compound by one, two, three, or more dots placed above the symbol of the element

---

[1] See *Annals of Philosophy*, **3**, 51, 363 [1814]; also first German edition of Berzelius' *Lehrbuch der Chemie*, vol. iii. p. 107 [1827].

[2] Such words as *oxygenium, nitrogenium, phosphoricum,* and *cobalticum* are taken by Berzelius to be the Latin names of elements.

[3] For a time Berzelius used the symbol Po for potassium; at a later date the symbol K (from *Kalium*) was substituted for Po.

wherewith the oxygen was combined: thus, he expressed the composition of potash alum by the symbol $\overset{\smile}{K}\overset{..}{S}^3 + \overset{..}{Al}\overset{...}{S}^3 + 24\overset{.}{H}$; when this symbol is written more fully it becomes

$$K\overset{\smile}{O}3SO^3 + Al^2O^23SO^3 + 24H^2O.\text{[1]}$$
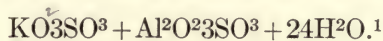
The Berzelian system of notation was soon used by all chemists. Turner used it in the fourth edition of his *Elements of Chemistry* (published in 1832–33), with the apologetic remark that he "ventured to introduce chemical symbols as an organ of instruction."

Changes have been made since the time of Berzelius in the use of the sign of addition, the employment of brackets, and the like, and many subsidiary signs have been introduced to express the prevailing notions regarding the arrangements of atoms in molecules, especially of organic compounds; but the foundations of the modern system of notation are those which were laid by the great Swedish chemist.

---

[1] At the time when Berzelius wrote the symbols given in the text, he was accustomed to use *barred symbols*, such as A̶ and H̶, to represent double atoms.

PART II.

THE HISTORY OF THE ATTEMPTS TO ANSWER THE QUESTION, WHAT HAPPENS WHEN HOMOGENEOUS SUBSTANCES INTERACT?

INTRODUCTORY REMARKS.

CHEMISTRY is concerned primarily with the study of material changes, and it was in the progress of the examination of these changes that the notion of homogeneous substances slowly took shape. Although it is convenient to keep separate the two fundamental questions of chemistry, when we are reviewing the progress of the science, it is impossible to make the separation complete. The two questions, What is a homogeneous substance? and, What happens when homogeneous substances interact? and the answers to these questions, constantly overlap. Hitherto I have been tracing, in the main, the history of the answers which have been given to the first question; I must now consider the answers which have been given to the second question.

What happens in the reaction between the elements hydrogen and oxygen whereby the compound water is produced? To answer this question, it is necessary to discover and set in order: (1) the relations between the quantities of the homogeneous substances which interact and between these and the quantity of the homogeneous substance which is produced, (2) the relations between the properties of all the substances concerned in the interaction, using the word *properties* in its widest meaning;

198

(3) the resemblances and differences between the substances concerned in this process of change and other homogeneous substances; (4) the conditions of temperature, pressure, and so on, under which the change occurs; or, one may say, the phenomena which accompany the transformation of hydrogen and oxygen into water; and (5) the resemblances and differences between the whole transaction which is being studied, and other transactions which are more or less like it.

In considering the answers which have been given at different times to the question, What is a homogeneous substance? it has been necessary to deal, in the first part of this book, with the discovery of the relations between the quantities of homogeneous substances which interact, and between these quantities and those of the products of the interactions; it has been necessary to include the consideration of certain portions of the answers which have been given to the second fundamental question of chemistry, What happens when homogeneous substances interact? The fuller answers to the second question which are now to be considered may evidently be divided into two groups: we have to consider the history of the study of the relations between the properties of homogeneous substances, and of the classification of these substances; and, secondly, the history of the elucidation of the phenomena which are bound up with chemical changes, and of the general comparison and contrast of chemical transactions.

The main purpose of the section of this book which now begins is to trace the history of the classification of homogeneous substances. The next section, which completes the book, deals with the history of the general laws of chemical change, and the history of the investigation of the relations between chemical changes and the physical phenomena which accompany them.

Inasmuch as every chemical inquiry presents two aspects, inasmuch as it is at once a study of reactions and a study of composition, it follows that a review of the systems of classification of homogeneous substances which have prevailed at different times will be concerned with those classifications of these substances which have been based chiefly on reactions, those classifications which have been founded mainly on com-

position, and those which have attempted to arrange homogeneous substances on the ground of connexions between composition and reactions. But no sharp lines of division have been drawn, or can be drawn between the three systems of classification.

THE HISTORY OF THE CLASSIFICATION OF HOMO-GENEOUS SUBSTANCES.

CHAPTER VIII.

ACIDS; BASES; SALTS. ACID-FORMING AND BASE-FORMING ELEMENTS. ACIDIC AND BASIC OXIDES.

THE general purpose of this book is to bring before the reader the main lines of movement which stand out clearly when we look at the progress of chemistry from the position now reached by the science. This purpose will be best served, if, in reviewing the history of the classification of homogeneous substances, I select those classes which are now thought to be especially important. I begin, therefore, with the division of certain compounds into acids, bases, salts, acidic and basic oxides. The differentiation of these classes of compounds carries with it the distinction between acid-forming and base-forming elements. I shall then sketch, in a broad and general manner, the development of the principles which have guided the classification of organic compounds. That will lead to a consideration of some of the attempts which have been made to include all homogeneous substances in one general scheme of classification, more particularly that scheme which is based on the generalization known as *the periodic law*.

The Greek word ὀξύς = acid is closely related to the word which was applied by the Greeks to vinegar. Similarly, the Latins used the words *acidus* (acid) and *acetum* (vinegar).

The fact that calcareous earths effervesce and dissolve when vinegar is poured on them is noted by many ancient authors. As many other liquids also dissolved calcareous earths, with effervescence, these liquids were gradually placed in the same category and called *acids*, and the prominent characteristic of this class of substances was their solvent power. Great stress was laid by the alchemists on the importance of acids, because one of the foundations of their system was the (alleged) necessity of dissolution, or destruction, as the antecedent of restoration and the development of more perfect life.

The detergent properties of ashes have been known and used from very ancient times. Pliny notes the use of *nitrum* for dissolving oils and sulphur, and making glass; he mentions that this substance changes the colour of green plants, and he says that a similar substance is obtained from wood-ashes. Substances which have these properties gradually came to be classed together under the name *alkali* (from the Arabian, signifying *the ash*).

The importance of the reactions between acids and alkalis was much dwelt on in the seventeenth century. Stress was laid on the fact that the properties of acids and of alkalis disappeared when these substances were mixed, so that the products did not affect the colours of plants, and had neither detergent nor solvent powers. These products came to be called *salts*, and to be regarded as distinct substances.

The word *salt* has been used for many centuries, certainly from the seventh century. In the older times it was employed as a class-name for substances like sea-salt. That substance was called *salt*, because, according to some authors, it is obtained by the action of the sun (*sol*) on sea-water, according to others, because it decrepitates in the fire (*exsilire* = to crackle and spring about). The alchemists used the word as the name of one of their three hypothetical principles, *sulphur*, *salt*, and *mercury*, none of which was a substance in the modern meaning of that term.

Boyle (towards the end of the seventeenth century) said that acids (1) dissolve very many substances, (2) precipitate sulphur from solutions thereof in alkalis, (3) change many

vegetable blues to reds, and (4) lose these characteristic properties when they are brought into contact with alkalis. Boyle noticed that only some alkalis effervesced with acids, although all lost their characteristic properties when they were mixed with acids. A vague and indefinite distinction began to be drawn between those alkalis which effervesced, and those which did not effervesce with acids, and this led to the use of the word *earths*, for substances which more or less resembled alkalis, but did not effervesce when mixed with acids.

In 1744 Rouelle introduced the term *base* to include alkalis, earths, metals, and certain oils. His notion was that a salt is constructed on the foundation of an alkali, earth, metal, or oil, by the addition thereto of an acid.

In a communication, *Sur les sels neutres*, made to the *Académie des Sciences* in 1754, Rouelle said, "J'ai étendu le nombre des sels autant qu'il était possible, en définissant génériquement le sel neutre, un sel formé par l'union d'un acide avec une substance quelconque, qui lui sert de base et lui donne une forme concrète ou solide."

Before accurate knowledge could be attained regarding the relations of acids, alkalis, salts, and bases, it was necessary to investigate these substances quantitatively; it was necessary to determine the compositions of many members of each class, and to measure the quantities of the substances which interacted.

A very important memoir, which laid the foundations of the quantitative study of the relations between acids, alkalis, and salts, was published by Joseph Black in 1755.[1] Black proposed to examine "the nature of *magnesia alba*, and especially to compare its properties with those of the other absorbent earths, of which there appeared to me to be very different kinds, although commonly confounded together under one name." He prepared *magnesia alba* by mixing solutions of Epsom salt and pearl ashes, boiling and washing the precipitated solid with cold water. He dissolved this magnesia in various acids, and examined "the neutral saline liquors" thus produced; Black concluded that "*magnesia* appears to be a substance very different

---

[1] *Experiments upon Magnesia alba, Quick-lime, and other Alcaline Substances.* By Joseph Black, M.D., Professor of Chemistry in the University of Edinburgh. (1766–1797.) Republished as No. 1 of the *Alembic Club Reprints.* [William F. Clay, Edinburgh, 1893.]

from those of the calcareous class, under which I would be understood to comprehend all those that are converted into a perfect quick-lime in a strong fire." Nevertheless, it was possible that magnesia might be a calcareous earth; therefore Black set about finding out whether magnesia could be "reduced to a quick-lime." He heated a weighed quantity of magnesia "to such a heat as is sufficient to melt copper"; the magnesia lost seven-twelfths of its weight; the calcined magnesia dissolved in acids "without any the least degree of effervescence," and produced salts which were qualitatively the same as those formed by the action of the same acids on uncalcined, or *mild* magnesia. He then heated a weighed quantity of mild magnesia in a retort, and obtained only a little water: "We may therefore safely conclude that the volatile matter lost in the calcination of *magnesia* is mostly air; and hence calcined *magnesia* does not emit air, or make an effervescence when mixed with acids." Black calcined a couple of drams of magnesia, dissolved the solid in "spirit of vitriol," added alkali, and obtained one dram and 50 grains of magnesia, having all the properties of this substance before calcination. The weight of the magnesia obtained was about 8 per cent. less than the weight of the magnesia which was calcined. Knowing that *alkali* contained fixed air,[1] Black concluded that the air which the calcined magnesia gained was furnished by the alkali, and that the acid which was joined to the magnesia (in this case, sulphuric acid) forced the air to separate from the alkali.

The next question which Black proposed to answer experimentally was, What quantity of air is expelled by acids from an alkali or from magnesia? He added a weighed quantity of oil of vitriol, diluted with water, to a weighed quantity of "a pure fixed alkaline salt,"[1] in a weighed flask, until "the salt was exactly neutralized," and then weighed the flask and its contents. He performed similar experiments with mild magnesia, and with the calcined magnesia obtained from a weighed quantity of mild magnesia. The calcined magnesia required about one per cent. less acid to saturate it than was required by the mag-

---

[1] When Black speaks of *alkali*, or *alkaline salt*, he means what we now call a carbonate of an alkali metal.

nesia before calcination; because, Black said, a little of the "fixed earth" of the magnesia was carried off with the air and water evolved during calcination. Black concluded that *mild magnesia* differs from *calcined magnesia* in containing a considerable quantity of air; and that *magnesia alba* (or *mild magnesia*) is a compound of "a peculiar earth" with fixed air. He then experimentally compared magnesia with other "absorbent earths," especially with chalk, showing that chalk dissolves in acids with effervescence, and is obtained again by adding alkali [1] to the solution. Black concluded that probably *crude lime* (or chalk) is a compound of quicklime and fixed air, and that if quicklime was dissolved in water, and alkali (carbonate of an alkali metal) was added, crude lime (chalk) would be precipitated, and corrosive, or caustic alkali would remain in solution.

Black stated five propositions which, he said, contained the most important consequences that followed from the account he had given of the relations between mild and caustic lime, and mild and caustic alkalis.

(1) Caustic lime, or caustic alkali, must weigh less than the mild lime, or mild alkali, from which it is obtained by calcination; and the caustic lime, or alkali, must saturate the same quantity of an acid as is saturated by the mild lime, or alkali, from which it has been obtained.

(2) Lime-water added to mild alkali must produce mild lime. When a weighed quantity of mild lime is calcined, and the residue is dissolved and mixed with mild alkali, the original weight of mild lime must be obtained.

(3) "If it be supposed that slaked lime does not contain any parts which are more fiery, active, or subtile than others, and by which chiefly it communicates its virtues to water, but that it is a uniform compound of lime and water, it follows, that as part of it can be dissolved in water, the whole of it is also capable of being dissolved."

(4) Caustic alkali, free from lime, should be produced by adding to a mild alkali that quantity of quicklime which is "just sufficient to extract the whole air of the alkali."

---

[1] When Black speaks of *alkali*, or *alkaline salt*, he means what we now call a carbonate of an alkali metal.

(5) If caustic alkali is added to magnesia dissolved in acid, "a magnesia free of air, or which will not effervesce with acids," should be obtained. And, if caustic alkali is added to a solution of *calcareous earth* in acid, slaked lime "destitute of air" should be formed.

Black then records the results of experiments whereby he proved the accuracy of these five propositions. His proofs of the first, second, and third propositions were, of course, furnished by quantitative experiments; the results were well within the limits of the experimental errors inherent in the methods of estimation known to Black.

The following are examples of Black's results:

(1) Two drams (120 grains) of chalk required 421 grains of diluted "spirit of salt" to saturate it; the quicklime obtained by calcining 2 drams of chalk required 414 grains of the same diluted "spirit of salt" to saturate it.

(2) Two drams (120 grains) of chalk were calcined; the quicklime thus formed, weighing 68 grains (120 grains pure chalk should give 67·2 grains quicklime), was thrown into an aqueous solution of "fixed alkaline salt," and one dram and 58 grains (118 grains) of chalk were obtained.

(3) Eight grains of quicklime, prepared by calcining chalk, dissolved almost completely in water; the residue weighed between one-third and one-half of a grain; a part of the residue dissolved in *aqua fortis* with effervescence, hence Black concluded that it was unchanged chalk; as the portion insoluble in *aqua fortis* was an ochry powder, Black concluded it to be "only an accidental or foreign admixture."

Black's "*experiments upon magnesia alba, quicklime, and other alcaline substances*" proved that the change of composition which accompanies the transformation of a mild to a caustic alkali is the same as that which accompanies the transformation of a mild earth to a quicklime, and consists in the removal of fixed air. These experiments established the characteristic reactions of the four classes of compounds, mild alkalis, caustic alkalis, mild earths, and quicklimes (that is, mild earths deprived of their fixed air). Black's examination of the qualitative reactions of the salts formed by saturating mild and caustic alkalis, and mild earths and quicklimes, with the same acid, advanced the study of salts as a class, by showing that the same salt may be formed by the interaction of an acid with two different compounds. These experiments supported and made more definite Rouelle's notion of a salt as a compound formed

by adding an acid to a base, and, indirectly, his application of the term base to substances which would not be placed in the same class when considered from the point of view of their composition, or from that of their reactions with substances other than acids. The experiments of Black made more definite the whole problem of the relations between acids, alkalis, and salts, and indicated the lines along which the investigators of this problem must proceed. Finally, Black's researches form an important advance towards the attainment of the essential object of chemistry, namely, the elucidation of the connexions between changes of composition and changes of properties of homogeneous substances.

The examination of alkalis, and substances allied to them, which was made before the discovery of oxygen (in 1774) enabled chemists in the early seventies of the eighteenth century to think of these substances, and their relations to one another, somewhat as follows: The name *caustic alkalis* (or, more simply, *alkalis*) was given to substances which dissolve easily in water to form liquids which are corrosive, and change certain vegetable colours, and react with acids, without effervescence, to form salts. *Mild alkalis* were those substances which produce fixed air, besides salts, when they react with acids, and in other respects resemble the caustic alkalis. Those substances which are only slightly soluble in water and react with acids, without effervescence, to form salts, were called *earths*. The name *mild earths* was applied to substances which are insoluble, or nearly insoluble in water, and react with acids to produce salts and fixed air. To each caustic alkali there corresponds a mild alkali, and to each earth a mild earth; the mild alkali, or the mild earth, is a compound of the caustic alkali, or of the earth, with fixed air. *Calces of metals* were those substances which are produced by calcining metals, and react with acids to produce salts. The name *acids* was given to liquids, and to solutions of gases and solids in water, which dissolve many substances, and react with alkalis, earths, metallic calces, and metals, to form salts. Finally, *salts* were thought of as those products of the interactions of acids and alkalis, acids and earths, acids and metallic calces, and acids and

metals, which have none of the distinctive characters of the substances by whose interactions they are formed.

Some chemists, notably Rouelle, employed the word *base* to include metals, metallic calces, earths, and alkalis, that is, all substances which produce salts by reacting with acids.

Looking back, I think we may see that the investigation of acids, bases and salts might have proceeded in two directions. Measurements might have been made of the quantities of acids and bases which react, in order that the quantitative relations between these substances should be determined. More searching examinations might have been made of the changes of composition which happen when salts are formed by the interactions of acids and bases, in order that light should be thrown on the qualitative relations of these substances. As a matter of fact, investigation proceeded in both directions. I propose now to describe some of the most important studies which were made of the compositions, and, therefore, also of the interactions of acids, bases and salts. An account will be given in another chapter of the main lines of advance in the examination of the quantitative relations of these classes of substances. (See Chapter X.)

The advances which are now to be considered were made along three lines: the compositions and reactions of acids were examined, or, we may say, that the nature of acids was examined; investigations were made of the nature of alkalis and earths; the nature of metallic calces was inquired into. These advances carried with them a clearing of ideas about salts, and had also a direct bearing on the classification of elements.

In 1777, Lavoisier gave the name *oxygen* to the gas which Priestley had called dephlogisticated air. Lavoisier was of opinion that oxygen is a constituent of all compounds which have the characteristic properties of acids, and that these properties are caused by the presence of this common constituent. He connected the particular character of each acid with the substance, or substances which combined with oxygen to produce that acid; and he said that the non-oxygenated part

of an acid is generally one, or more than one of those elements which we now call non-metals.[1]

Those who framed the nomenclature introduced in 1787, of whom Lavoisier was one, spoke of acids as compounds of oxygen with *simple*, or *compound acidifiable bases*;[2] they placed most of the mineral acids in the class of oxygenated compounds of simple acidifiable bases, and they classed the vegetable and animal acids as oxygenated compounds of compound acidifiable bases. The simple acidifiable bases known in 1787 were carbon, nitrogen, phosphorus, and sulphur; the compound acidifiable bases included the *tartaric radical*, the *muriatic radical*, and the like. The application of the Lavoisierian conception of acid may best be illustrated by tracing the chemical history of one particular acid, namely, the substance now called hydrochloric acid, and certain substances related thereto.

More or less impure aqueous solutions of this acid have been used in chemical operations for many centuries. The acid liquor was generally called *spiritus salis* by the alchemists and early chemists. Priestley prepared impure specimens of the gaseous compound in 1772, and named it *marine acid gas*. The authors of the new nomenclature introduced in 1787 (see Appendix to Part I, pp. 190, 191) adopted the name *acide muriatique*, from the Latin *muria* = salt.

In 1774, Scheele described several reactions of a new yellow gas, with a very suffocating odour, which he had prepared by digesting marine acid with *manganese* (manganese dioxide).[3] As Scheele supposed that phlogiston was removed from the marine acid by the manganese, he named the new gas *dephlogisticated marine acid*. He said that the gas "unites with water in very small quantity; and gives the water a slightly acid taste; but as soon as it comes in contact with a combustible matter, it becomes again a proper marine acid."[4]

---

[1] *Mémoire sur l'existence de l'air dans l'acide nitreux;* and *Considérations générales sur la nature des acides.* [1777.]

[2] The difference should be noticed between the meaning given to the word *base*, which was used to denote a substance, or collocation of substances, that forms an acid by combining with oxygen, and the meaning given to the same word by Rouelle.

[3] *Kong. Vetenskaps Academiens Handlingar*, **25**, 89 [1774].

[4] Quoted from No. 13 of the *Alembic Club Reprints* (entitled *The Early History of Chlorine*), which contains translations of portions of Scheele's memoir, and other memoirs by Berthollet, G. de Morveau, and Gay-Lussac and Thenard.

As Lavoisier supposed that all acids are compounds of oxygen with acidifiable bases, simple or compound, he regarded muriatic acid to be composed of oxygen and a hypothetical substance which he named *base muriatique,* or *radical muriatique.* Lavoisier sought eagerly, but unsuccessfully, to isolate this radical. He said that Scheele's dephlogisticated marine acid was formed by the combination of muriatic acid with oxygen; that the addition of a second dose of oxygen made the acid more volatile but less soluble in water, imparted to it a more penetrating odour, but diminished its acidic qualities. Lavoisier was inclined at first to name the original acid, and the product of its oxidation, *acide muriateux* and *acide muriatique,* respectively (on the analogy of *acide sulfureux* and *acide sulfurique*); but he said that it was advisable to give an exceptional name to the more oxidized acid, because it was very unlike any other known acid; therefore he called it *acide muriatique oxygéné.* Lavoisier obtained oxygenated muriatic acid by heating certain metallic oxides with muriatic acid; he supposed that the oxides lost oxygen which combined with the muriatic acid.

Berthollet examined dephlogisticated marine acid in 1785.[1] After describing some of its reactions, or rather the reactions of an aqueous solution of the gas, he said: "We can therefore . . . regard dephlogisticated marine acid as almost deprived of acidity." Berthollet prepared the gas by acting on *manganese* with marine acid; he then removed some of the *vital air* (oxygen) of *manganese* by calcining it, and when he now added marine acid, he obtained "a much smaller quantity of dephlogisticated marine acid." He concluded that "it is . . . to the vital air of the manganese, which combines with the marine acid, that the formation of the dephlogisticated marine acid is due." Berthollet met the objection that marine acid does not combine with "vital air in the elastic state," by saying that the affinity between the acid and the air is so small that these substances cannot combine "except by double affinities," and that "the elastic state of a fluid is an obstacle to combination." Although he was unable to effect the combination of marine acid and

---

[1] *Mém. de l'Académie royale* for 1785, 276. The quotations in the text are taken from the *Alembic Club Reprints,* No. 13 (see note, p. 209).

oxygen, Berthollet supposed he had succeeded in decomposing dephlogisticated marine acid into muriatic acid and oxygen; for, exposing a saturated aqueous solution of the gas to sunlight, he obtained *vital air* (oxygen), and found ordinary marine acid in the water. "It is vital air, then," Berthollet said, "which disguises the properties of dephlogisticated marine acid; it loses them as soon as that principle separates from it." In another place in this memoir Berthollet refers to oxygenated muriatic acid as "disguised marine acid."

Scheele's experiments had shown that the salts obtained by dissolving certain metals in aqueous solutions of dephlogisticated marine acid are, very probably, the same as those produced by dissolving the metals in aqueous marine acid. This is what one would expect, Berthollet said. "Chemists agree," he remarked, "that the metals are reduced to calces when they are dissolved by means of marine acid, and consequently that they are combined with vital air." As the marine acid is not decomposed, Berthollet argued, the metals must get vital air from the water; that they decompose some of the water which is present, is proved by the fact that inflammable air is produced; but when a metal dissolves in (an aqueous solution of) dephlogisticated marine acid, all it has to do is to take vital air from the acid, and then the calx combines with the marine acid which is there when vital air has been taken away; that the metals do act thus is proved by the fact that inflammable air is not produced.

According to Guyton de Morveau,[1] dephlogisticated marine acid is changed to marine acid by causing it to combine with inflammable air (hydrogen); Berthollet failed to effect the union of the gases by agitating a mixture of them over water.

In 1800, Henry [2] obtained hydrogen by the action of "electric shocks" on muriatic acid; but, as he could not obtain more than about 7 volumes of hydrogen from 100 volumes of muriatic acid gas, he concluded that the hydrogen came from the small quantity of water which, he said, he could not separate from the acid. In 1809,[3] he obtained a little oxygenated muriatic acid

---

[1] *Dictionaire de Chimie*, p. 251.   [2] *Phil. Trans.* for 1800, 188.
[3] *Phil. Trans.* for 1809, 430.

by passing "electric shocks" through a mixture of muriatic acid and oxygen; he accounted for this by supposing that the electric discharge decomposed some of the water, which he was unable to remove from the muriatic acid, into hydrogen and oxygen, and that the oxygen combined with muriatic acid and produced oxygenated muriatic acid. Henry came to the conclusion that "the really acid portion of muriatic acid does not sustain any decomposition by the action of electricity."

Henry insisted that it was impossible to make a complete separation of muriatic acid and water. Every one who investigated this acid during the first few years of the nineteenth century asumed that muriatic acid cannot exist except in combination with water or a base.

Gay-Lussac and Thenard [1] thought that muriatic acid must contain water, "intimately combined," or, "at least, the principles which constitute water," in the same proportion as in water, because they obtained water by passing muriatic acid gas over dry, heated litharge. They attempted to estimate the quantity of water in muriatic acid, and came to the conclusion that the gaseous acid contained one fourth of its weight of water, and that the water could not be removed, directly, without the decomposition of the acid itself. They hoped to obtain dry muriatic acid gas by removing the oxygen from oxygenated muriatic gas "by means of combustible bodies," because "we had found," they say, "that oxygenated muriatic gas does not contain combined water." But they were unable to remove oxygen from oxygenated muriatic gas even when they used charcoal "urged to the most violent heat of the forge." We shall see (p. 216) that Davy also made this experiment, and concluded from the negative results that oxygenated muriatic acid probably does not contain oxygen.

The methods which Gay-Lussac and Thenard used for determining the water in muriatic acid are interesting, and show the firm hold of the Lavoisierian theory of acids on the minds of chemists of the time. They dissolved in cold water a weighed quantity of muriatic acid gas, added nitrate of silver,

---

[1] *Mém. de la Soc. d'Arcueil*, **2**, 295 [1809]. A translation of parts of this memoir and portions of other memoirs by the same authors is given in No. 13 of the *Alembic Club Reprints*. The quotations in the text are taken from this translation.

and weighed the muriate of silver which was precipitated; they calculated the weight of muriatic acid contained in this quantity of muriate of silver from what they say was known to be the composition of that salt, and set down as water the difference between this weight and that of the muriatic acid wherewith the experiment was begun. The composition of muriate of silver is given by Gay-Lussac and Thenard as 100 of silver combined with 7·6 of oxygen and 25·71 of acid. They say that the quantity of oxygen in the water which they had determined to be present in muriatic acid gas was "very nearly enough to produce the oxide [of silver] necessary for the saturation of the acid combined with it." They confirmed the result of their estimation of water by proving that when muriatic acid gas was passed over heated iron, the whole of the iron which was acted on was changed to muriate of iron, and hydrogen was disengaged; this result, they say, "proves that the muriatic gas contained exactly enough water to oxidize all the iron which it could dissolve."

Gay-Lussac and Thenard also assert that they found (1) oxygenated muriatic gas to contain "exactly the half of its volume of oxygen gas," by decomposing it by "ammoniacal gas," and (2) oxygenated muriatic gas to combine with its own volume of hydrogen and form "ordinary muriatic gas," without the deposition of any water. From the specific gravities of oxygenated muriatic gas, oxygen, and hydrogen, and the fact that oxygen combines with twice its volume of hydrogen to form water, they calculated (1) the weight of oxygen in a determinate volume (of known weight) of oxygenated muriatic gas, (2) the weight of hydrogen required to combine with this weight of oxygen in order to form water, and, by adding (1) and (2), they found (3) the weight of water which (by their hypothesis) was produced when oxygenated muriatic gas and hydrogen combined to form muriatic acid. But this quantity of water was assumed by Gay-Lussac and Thenard to combine with the muriatic acid which was formed: now the weight of muriatic acid formed was equal to the sum of the weights of oxygenated muriatic gas and hydrogen which combined; therefore, their argument ran, they had determined the weight of water which was combined with a determinate weight of muriatic acid gas.

Gay-Lussac and Thenard then recalled Berthollet's observation that dry oxygenated muriatic gas is not changed by light, but the gas is at once decomposed by light when water is present, with the formation of muriatic acid and oxygen; and they concluded that the gas would probably be decomposed by water and heat acting together. They tried the experiment, and found that muriatic acid and oxygen were produced when oxygenated muriatic gas and steam were passed through a heated porcelain tube. They then brought a piece of iron heated to 150° into a mixture of equal parts of oxygenated muriatic gas and hydrogen; at once there was "violent inflammation, and production of muriatic acid." They explained the results of these experi-

ments by sayng that the affinity of muriatic acid for water is very great; and therefore, in the first experiment, the muriatic acid leaves the oxygen, wherewith it is combined in oxygenated muriatic gas, and combines with water, at a moderate temperature; and, in the second experiment, water is formed by the removal of oxygen from the oxygenated muriatic acid, because the reaction also produces muriatic acid which is eager to combine with water. They then proved that a mixture of equal volumes of oxygenated muriatic acid and hydrogen did not change in the dark, but was soon transformed into muriatic acid in feeble sunlight, and exploded violently in bright sunshine.

"The experiments which we have reported up till now," Gay-Lussac and Thenard remark, "ought to give an idea of the constitution of oxygenated muriatic gas quite different from that which had been formed of it. It had been regarded as a most easily decomposed body, and we see, on the contrary, that it resists the action of the most energetic reagents, and that it is only with the help of water or of hydrogen that muriatic acid can be extracted from it in the state of gas."

The next experiment made by Gay-Lussac and Thenard was to heat a mixture of muriate of silver (which had been fused) and charcoal (which had been very strongly heated): there was little or no action; but when ordinary moist charcoal was used, silver was formed and abundance of muriatic acid gas was disengaged. That is, Gay-Lussac and Thenard said, muriatic gas was not produced "except when the water necessary for its gaseous constitution could be formed."

Gay-Lussac and Thenard concluded their memoir by saying:

"Oxygenated muriatic acid is not decomposed by [dry] charcoal, and it might be supposed, from this fact and those which are communicated in this memoir, that this gas is a simple body. The phenomena which it presents can be explained well enough on this hypothesis; we shall not seek to defend it, however, as it appears to us that they are still better explained by regarding oxygenated muriatic acid as a compound body."

In their *Recherches Physico-chimiques* (Paris, 1811), Gay-Lussac and Thenard summarized their experiments, and also some of those made by Davy, which, they said, could be explained on the supposition that oxygenated muriatic acid is a simple substance; they, however, preferred the hypotheses that muriatic acid is a compound of an unknown base, or radical,

with water, and oxygenated muriatic acid is a compound of oxygen with the same base.

Early in the nineteenth century, Davy began to use "the new powers and methods arising from the applications of electricity to chemistry," for the purpose of "extending our knowledge of the principles of bodies." In the Bakerian lecture delivered in December, 1808, he described his earlier experiments on muriatic acid gas.[1] Davy obtained hydrogen by the action of electricity, and also by the action of potassium, on the gas; but he attributed the production of hydrogen to the water which he had not been able to separate from muriatic acid. He tried to obtain dry muriatic acid gas by methods very similar to those used by Gay-Lussac and Thenard, but without success. Among other reactions, he examined that of phosphorus with oxymuriatic acid gas, hoping to obtain oxide of phosphorus and dry muriatic acid; but the products of the reaction were a solid and a liquid substance, which he was inclined to regard as, respectively, "a combination of phosphoric, and muriatic acid in their dry states," and "a compound of phosphorous acid, and muriatic acid, both free from water."[2] He endeavoured to elucidate the nature of these compounds by heating them with potassium; but his vessels were always broken by the violence of the reactions.

At this time, Davy thought that his experiments proved[3] that "muriatic acid gas is a compound of a substance which as yet has never been procured in an uncombined state, and from one third to one fourth of water, and that oxymuriatic acid is composed of the same substance, (free from water) united to oxygene."

Davy begins a memoir read to the Royal Society in July, 1810,[4] by saying:

"The illustrious discoverer of the oxymuriatic acid considered it as muriatic acid freed from hydrogene, and the common muriatic acid as a compound of hydrogene and oxymuriatic acid; and on this theory he denominated oxymuriatic acid dephlogisticated muriatic acid."

[1] *Phil. Trans.* for 1809, 39.
[2] Berthollet (*Mém. de la Acad. royale* for 1785, 276) had given the same account of the reactions between phosphorus and oxymuriatic acid: see *Alembic Club Reprints*, No. 13, pp. 25, 26.
[3] *Phil. Trans.* for 1809, 450.
[4] *Phil. Trans.* for 1810, 231.

Davy repeated an experiment made by Gay-Lussac and The-nard,[1] which showed that neither muriatic acid nor oxymuriatic acid is changed when heated to a high temperature with charcoal "which had been freed from hydrogene and moisture by intense ignition in vacuo."

"This experiment," Davy said, "which I have several times repeated, led me to doubt of the existence of oxygene in that substance, which has been supposed to contain it above all others in a loose and active state; and to make a more rigorous investigation than had hitherto been attempted for its detection."

The chemists who had examined the reactions of oxymuriatic acid supposed that the liquid produced by heating tin in that gas was a compound of oxide of tin and muriatic acid. Davy argued that oxide of tin should be obtained by adding ammonia to the liquid compound, if that supposition were correct; but he found that ammonia combined with the liquid and produced a solid substance, which volatilized completely when heated. Berthollet and others had examined the liquid, and the solid product of the reaction between phosphorus and oxymuriatic acid gas; the opinion which received the assent of most chemists was that one of these was a compound of muriate of ammonia and phosphoric acid, and the other a compound of muriate of ammonia and an acid of phosphorus containing less oxygen than phosphoric acid. Davy said that phosphate of ammonia would be produced by treating the first of these compounds with ammonia, if the generally accepted view of its constitution were correct; and that, when the product of the action of ammonia on the compound was heated, muriate of ammonia would volatilize and phosphate of ammonia remain. But experiments proved that the product of the action of ammonia on the compound in question did not change when strongly heated, and was acted on only by a few very energetic reagents.

Davy then performed various other experiments, and arrived at the conclusion that "no substance known to contain oxygene could be obtained from oxymuriatic acid," in the "modes of operation" he had employed.

Davy then turned to the experiment, recorded by Gay-

Lussac and Thenard, wherein muriatic acid was obtained without the deposition of water by causing oxymuriatic acid gas and hydrogen to combine. Davy confirmed this experiment, and made it more valuable by showing that equal, or almost equal volumes of hydrogen and oxymuriatic acid combine to form a volume of muriatic acid gas which is approximately equal to the sum of the volumes of the combining gases. Davy showed that the results of this experiment could not be used to prove either the presence of oxygen in oxymuriatic acid, or the presence of water in muriatic acid gas; for one of these statements was assumed to be true in every argument which used the experiment to prove the accuracy of the other. Gay-Lussac and Thenard supposed they had proved the presence of water in muriatic acid gas by the fact that water was obtained when the gas was passed over heated litharge. "It is obvious," Davy said, "that in this case they formed the same compound as that produced by the action of oxymuriatic acid on lead; and in this process the muriatic acid must lose its hydrogene, and the lead its oxygene; which of course would form water." At a later time, Davy examined quantitatively the reactions between oxides and muriatic acid whereby muriates and water are produced. In his *Elements of Chemical Philosophy* (published in 1812) he laid stress on the fact that, if water is obtained from muriatic acid gas, it is only by the reactions of substances which contain oxygen; and he said: "The quantity [of water] produced is exactly proportional to the oxygene contained in the substance and the hydrogene in the muriatic acid gas, and the other result is the same as the substance combined with the oxygene would produce directly by its action upon chlorine." [1]

Davy fully recognized the importance of proving, or disproving the existence of combined water in muriatic acid gas. If it was proved conclusively that the gas contains water, then certain experimental results—notably the complete disappearance of hydrogen and oxymuriatic acid when these combine to form muriatic acid gas—could be explained only by supposing that oxymuriatic acid contains oxygen. He therefore re-

---

[1] *Elements of Chemical Philosophy*, p. 250. In 1812 Davy had ceased to use the term *oxymuriatic acid*.

peated the experiments which had led him to suspect the
presence of combined water in muriatic acid. He found that
mercury completely decomposed a volume of muriatic acid gas,
producing calomel and about half a volume of hydrogen; and
that potassium, zinc, and tin also decomposed the gas, forming
muriates of the metals, and a volume of hydrogen approxi-
mately equal to half the volume of the muriatic acid gas em-
ployed.

"It is evident," Davy said, "from this series of observations, that Scheele's
view (though obscured by terms derived from a vague and unfounded general
theory), of the nature of the oxymuriatic and muriatic acids, may be con-
sidered as an expression of facts; whilst the view adopted by the French
school of chemistry, and which, till it is minutely examined, appears so
beautiful and satisfactory, rests in the present state of our knowledge, upon
hypothetical grounds."

Davy then described many of his own experimental results,
and also many of those established by Gay-Lussac and Thenard,
in terms of the hypothesis that oxymuriatic acid is a simple sub-
stance, and muriatic acid is a compound of this substance and
hydrogen; and then he demonstrated the simplicity, and direct
applicability to facts, of that hypothesis.

Most of those who had examined muriatic acid, and the sub-
stances allied to it, supposed that the acid combined with
oxygen in two proportions, forming oxymuriatic acid, and then
a compound which was known as *hyperoxymuriatic acid*, or
hyperoxygenized muriatic acid. Davy examined the salts called
hyperoxymuriates (we now call them *chlorates*) and showed that
there was no valid evidence in favour of the existence of a
peculiar compound of muriatic acid with a greater quantity of
oxygen than was supposed to be present in oxymuriatic acid.
If we keep to facts, Davy said, we must conclude that hyper-
oxymuriate of potash is not, as had been supposed, a compound
wherein muriatic acid exists combined with much oxygen, but
is merely "a triple compound of oxymuriatic acid, potassium,
and oxygene."

Davy concludes the memoir we are now considering (1810)
by discussing the general chemical relations of oxymuriatic
acid. Scheele, who discovered this substance, gave it a name
which placed it among acids, although the view he expressed

of its relations to other substances would be more accurately represented in modern chemical language by a name which should not assign it to any particular class of substances. Lavoisier's general conception of the cause of acidity obliged him to place oxymuriatic gas among the acids; and this position was confirmed by the fact that an aqueous solution of the gas dissolves metals, and produces the same salts as are formed by dissolving these metals in muriatic acid. From his experiments, made in 1785, Berthollet concluded that "dephlogisticated marine acid is almost deprived of acidity." Gay-Lussac and Thenard preferred to regard oxymuriatic gas as an acid, although they recognized that the facts they had themselves observed were in keeping with the view that it is a simple substance. In 1810 Davy said:

"Few substances, perhaps, have less claim to be considered as acid than oxymuriatic acid. As yet we have no right to say that it has been decompounded; and as its tendency of combination is with pure inflammable matters, it may possibly belong to the same class of bodies as oxygene. May it not in fact be a *peculiar* acidifying and dissolving principle, forming compounds with combustible bodies, analogous to acids containing oxygene, or oxides, in their properties and powers of combination; but differing from them, in being for the most part, decomposable by water? On this idea muriatic acid may be considered as having hydrogene for its basis, and oxymuriatic acid for its acidifying principle."

In another part of the same memoir Davy said:

"If . . . oxymuriatic acid gas be referred to the same class of bodies as oxygene gas, then, as oxygene is not an acid, but forms acids by combining with certain inflammable bodies, so oxymuriatic acid, by uniting to similar substances, may be conceived to form either acids, which is the case when it combines with hydrogene, or compounds like acids or oxides, capable of forming neutral combinations, as in the instances of the oxymuriates of phosphorus and tin."

It is interesting to notice that Davy (in 1810) calculated what we should now call the atomic weight of oxymuriatic acid (chlorine), and the molecular weight of muriatic acid, from the results of his analyses of potash (potassium oxide), and of his combustion of potassium in muriatic acid gas, basing his calculations on "the ingenious idea of Mr. Dalton, that, if hydrogene be considered as 1 in weight, in the proportion it exists in water, then oxygene will be nearly 7·5." Davy found the values 32·9 and 33·9 for the combining proportions of oxymuriatic acid and muriatic acid respectively.

In a memoir [1] read to the Royal Society in 1811, Davy described, in detail, experiments designed to establish the relations between the quantities which react of oxymuriatic acid and potassium, sodium, potash, and soda respectively, and the reacting quantities of muriatic acid and potash, and muriatic acid and soda. He also described similar experiments on the reaction of oxymuriatic acid with baryta, strontia, and lime. The results of these quantitative experiments convinced Davy that the products of the combination of oxymuriatic acid with the metals which he examined were identical with the products of the neutralization of the oxides of these metals by muriatic acid, and with the salts produced by heating these oxides in oxymuriatic acid gas.

He extended the inquiry to the determination of the quantities of oxymuriatic acid gas which combined with determinate weights of the following metals; antimony, arsenic, bismuth, copper, iron, lead, mercury, silver, tellurium, tin, and zinc; he examined the products of these combinations, and he compared his results with those which he obtained by heating the oxides of the same metals in oxymuriatic acid gas. Of the reactions between oxymuriatic acid and metallic oxides, Davy said: "In cases where oxygene was given off, it was found exactly the same in quantity as that which had been absorbed by the metal."

Davy summarized his results thus:

"Oxymuriatic acid combines with inflammable bodies, to form simple binary compounds; and in these cases, when it acts upon oxides, it either produces the expulsion of their oxygene, or causes it to enter into new combinations. If it be said that oxygene arises from the decomposition of the oxymuriatic gas, and not from the oxides, it may be asked, why it is always the quantity contained in the oxide; and why in some cases, as those of the peroxides of potassium and sodium, it bears no relation to the quantity of gas." "When potassium is burnt in oxymuriatic gas, a dry compound is obtained. If potassium combined with oxygene is employed, the whole of the oxygene is expelled, and the same compound formed. It is contrary to sound logic to say, that this exact quantity of oxygene is given off from a body not known to be compound, when we are certain of its existence in another; and all the cases are parallel." [2]

Davy proved, in this memoir, that dry oxymuriatic gas does not bleach dry blue litmus-paper, whereas the moist gas at once removes

---

[1] *Phil. Trans.* for 1811, 1.
[2] For the criticism of this argument made by Berzelius, see p. 222.

the colour of paper soaked in blue litmus solution.   "This experiment," Davy said, "seems to prove that . . . the operation of the gas in bleaching depends entirely upon its property of decomposing water, and liberating its oxygene."

Davy concludes this memoir by proposing the name *chlorine* (from χλωρός = yellow) for oxymuriatic acid, "a name founded upon one of its obvious and characteristic properties—its colour." "Should the substance hereafter be discovered to be compound," Davy remarks, "and even to contain oxygene, this name can imply no error, and cannot necessarily require a change." The reasons which induced Davy to propose the abolition of the name "oxymuriatic acid" are stated by him in the following words:

"To call a body which is not known to contain oxygene, and which cannot contain muriatic acid, oxymuriatic acid, is contrary to the principles of that nomenclature in which it is adopted; and an alteration of it seems necessary to assist the progress of discussion, and to diffuse just ideas on the subject. If the great discoverer of this substance had signified it by any simple name, it would have been proper to have recurred to it; but, dephlogisticated marine acid is a term which can hardly be adopted in the present advanced era of the science."

In a note Davy says:

"It is possible that oxymuriatic gas may be compound, and that this body and oxygene may contain some common principle; but at present we have no more right to say that oxymuriatic gas contains oxygene than to say that tin contains hydrogene; and names should express things and not opinions; and till a body is decomposed, it should be considered as simple."

In the same note, referring to a criticism of his work by "Mr. Murray, of Edinburgh," Davy remarks:

"This ingenious chemist has mistaken my views, in supposing them hypothetical; I merely state what I have seen, and what I have found. There may be oxygene in oxymuriatic gas, but I can find none."

It is instructive, as well as interesting, to know that Berzelius refused, for a time, to accept Davy's view that oxymuriatic gas is a simple substance. In 1813 Berzelius sent a letter "On the Nature of Muriatic Acid" to Thomson.[1] The letter was written, Berzelius said, "to promote discussion." Davy had laid great stress on the fact that the quantity of

---

[1] Thomson's *Annals of Philosophy*, **2**, 254 [1813].

oxygen produced in the reaction between oxymuriatic gas and a salifiable base is equal to the quantity of oxygen contained in the base; and on the facts that oxymuriatic gas is not decomposed by dry charcoal, or by dry muriate of silver, but it readily combines with metals.

Berzelius brought the first of these facts within the older hypothesis (that oxymuriatic gas is a compound of an unknown base and oxygen) by asserting that the weight of oxygen in a determinate quantity of a base is equal to one half of the oxygen in the weight of oxymuriatic gas which neutralizes that quantity of base, because this is the relation between the quantities of oxygen in the weights of bases and acids which neutralize one another; "and that, of consequence, the quantity of oxygen disengaged from the oxymuriatic gas decomposed by a saline base is equal to that contained in the base by which it is decomposed." The words used by Berzelius, "and that, of consequence," took for granted the accuracy of his hypothesis that muriatic acid is a compound of one atom of "a combustible radical still unknown" with two atoms of oxygen, and oxymuriatic gas is a compound of one atom of the same radical with three atoms of oxygen.

Berzelius met Davy's second group of objections to the older hypothesis by asserting that several acids exist only in combination with water, for example, sulphuric, nitric, oxalic, and tartaric acid; and, therefore, one might very well suppose that muriatic acid could exist only in combination with water. If this is granted, Berzelius said, "a combustible body, the oxide of which formed by the quantity of oxygen contained in the oxymuriatic gas, is insufficient to saturate all the quantity of muriatic acid contained in that gas, can never at any temperature whatever, decompose oxymuriatic gas into oxygen and muriatic acid, because the muriatic acid has no base with which it can combine in order to preserve its existence as an acid." [1] According to Berzelius, the combustible substance must take either all the oxygen of the oxymuriatic gas or none of it.

---

[1] The older hypothesis explained the actual existence of muriatic acid gas by supposing this substance to be a compound of the real acid with water acting as a base. In Berzelian language, the gaseous acid was "a muriate of water, without excess either of water or muriatic acid."

Oxide of carbon, Berzelius said, does not combine with any other oxide; "hence, carbon cannot furnish an oxide capable of uniting with muriatic acid when deprived of its excess of oxygen." Many metals combine with oxymuriatic gas because the oxides of them formed by removing oxygen from that gas exactly saturate the muriatic acid which remains.

Berzelius said he would prove "by the doctrine of definite proportions," that "there are combinations which, if explained according to the hypothesis of Davy, are inconsistent with well-ascertained chemical proportions." Berzelius applied the hypothesis that muriatic acid is a compound of an unknown base and oxygen to the numbers obtained by analyzing *submuriate of copper*, and to certain data regarding the quantities of oxide of copper and muriatic acid which neutralize each other, and showed that this led to a very simple relation between the number of atoms of muriatic acid, oxide of copper, and water, in the salt. He then professed to apply the new hypothesis to the same data, and to show that it led to the ratio of one atom of oxide of copper to three quarters of an atom of water in *submuriate of copper;* "that is to say," according to Berzelius, "that the water is to the base in a ratio inconsistent with the doctrine of definite proportions."

In reaching this conclusion, which is *not* "inconsistent with the doctrine of definite proportions," Berzelius assumed that all muriates must contain oxygen; and he, therefore, treated the analytical data so as to make them represent the formation of oxide of copper, and the combination of this oxide with chlorine: in other words, Berzelius did not apply Davy's hypothesis, but his own version of that hypothesis to certain analytical data. Berzelius says he was surprised that the new hypothesis "could ever gain credit." He asserts that this hypothesis will not allow the existence of a *muriate of potash;* for such a salt *must* contain both muriatic acid and potash, and the new hypothesis says it does not contain an acid, an oxide, or potash.

At this time Berzelius regarded salts to be compounds of acids with oxygenated compounds of metals, or of radicals. Berzelius accepted Davy's view of the composition of muriatic

acid, and admitted chlorine to be a simple substance, some time after the publication of Gay-Lussac's memoirs on prussic acid, in 1815.

It was generally thought by chemists in the early years of the nineteenth century that "a peculiar acid principle" existed in the salts then called *hyperoxymuriates*, and now called *chlorates*. Davy and Gay-Lussac had both examined these salts, and the gases produced by treating them with acids. In 1811, and 1814,[1] Davy published two memoirs on these compounds; and Gay-Lussac [2] stated his views regarding them in 1816. Davy came to the conclusion that the hyperoxymuriates are salts of an acid "which owes its acid powers to combined hydrogene." "All the new facts," he says, "confirm an opinion which I have more than once before submitted to the consideration of the Society, namely, that acidity does not depend upon any *peculiar* elementary substance, but upon *peculiar arrangements* of various substances." [3] Gay-Lussac combated this view. He said it was an hypothesis to assert, as Davy asserted, that chlorate of potash is a *triple* compound of chlorine, oxygen, and potassium. He affirmed that the strongest analogies show this salt to be a *binary* combination of one molecule of potash and one molecule of chloric acid.

Gay-Lussac, about 1815, thought of salts as formed by the union of an acid and a base, and as containing the acid and the base. He regarded the constitutions of the salts of such acids as sulphuric, nitric, and oxalic, to be analogous to the constitutions of the acids themselves, inasmuch as both the salts and the acids were considered by him to be compounds of the anhydrous acids with bases; in the cases of the acids, the base was water. The view upheld by Gay-Lussac was generally accepted in the second decade of last century; but, after Davy had proved muriatic acid to be a compound of hydrogen and chlorine, and the salts of this acid to be compounds of metals and chlorine, it was impossible to apply to all acids the view championed by Gay-Lussac. The work which was done by that chemist on

---

[1] *Phil. Trans.* for 1811, 155; *Phil. Trans.* for 1815, 214.

[2] *Annal. Chim. Phys.*, [2] **1**, 157 [1816].

[3] No. 9 of the *Alembic Club Reprints* (On *The Elementary Nature of Chlorine*) contains Davy's most important memoirs on muriatic and oxymuriatic acids.

hydriodic acid and prussic acid negatived his own notion of acids as compounds of certain radicals with water, and established the existence of two acids which did not contain oxygen and were similar in composition to muriatic acid.

Gay-Lussac's memoir on iodine, which was published in 1814, is one of the most complete and able investigations of the chemical relations of an element and its compounds which has ever been made.[1]   We are concerned at present with that part of it which deals with hydriodic acid.

Gay-Lussac prepared hydriodic acid gas and hydriodic acid in aqueous solution; he proved the acid to be a compound of equal volumes of hydrogen and gaseous iodine; he determined the relative density of the gaseous acid, and also its gravimetric composition; he prepared, described, and analyzed many of the salts of hydriodic acid, and he gave an exhaustive description of the reactions of the acid and its relations to those substances wherewith it is allied.   In this memoir Gay-Lussac said:

"As the acids which chlorine, iodine, and sulphur form with hydrogen have the characteristic properties of acids formed by oxygen, they must be placed in the same class as these, the class to which is given the common name *acids;* but, in order to distinguish the acids in question, I propose to prefix the syllable *hydro* to the special name of the acid under consideration, so that the acidic compounds of hydrogen with chlorine, iodine, and sulphur will be named hydrochloric, hydriodic, and hydrosulphuric acid; the acidic compounds of oxygen with these substances will be called chloric, iodic, etc., acid, in accordance with the ordinary usage."

In his *Recherches sur l'acide prussique,* published [2] in 1815, Gay-Lussac prepared liquid prussic acid, proved it to be composed of hydrogen, carbon, and nitrogen, analyzed it quantitatively, determined the relative density of the compound in the state of gas, and studied the chemical relations of the acid.   Gay-Lussac said that the acidic properties of this compound could not depend on the presence of hydrogen, as that element (he asserted) is very alkaline, but did depend on the carbon and nitrogen which the acid contains.   He considered prussic acid to be a true hydracid, wherein carbon and nitrogen replace the chlorine of hydrochloric acid, the iodine of hydriodic acid, and the sulphur of hydrosulphuric acid.

[1] *Annal. Chim. Phys.,* **91,** 5 [1814].
[2] *Ibid.,* **95,** 136 [1815].

By heating potassium in gaseous prussic acid, Gay-Lussac proved that the gas contains half its volume of hydrogen, which is replaced by potassium (as the hydrogen of hydrochloric acid is replaced by the same metal), with the formation of a compound of potassium with the carbon and nitrogen of the acid. Gay-Lussac said that the carbon and nitrogen formed what he called *le radical prussique*, and afterwards named *cyanogene* (from κυανος = blue, and γεννάω = I produce). In accordance with this view of the constitution of the compound, he proposed for it the name *l'acide hydrocyanique*, and the salts of this acid he named *hydrocyanates*. He obtained cyanogen gas (by heating dry cyanide of mercury), analyzed it, and determined its vapour-density. Of this substance he says it is "a remarkable example, and at present a unique example, of a body which, although a compound, plays the part of a simple body in its combinations with hydrogen and with the metals."

Lavoisier taught that acids are compounds of oxygen with simple acidifiable bases, or with compound acidifiable bases, and salts are combinations of acids with salifiable bases. Chemists, notably Davy, gradually arrived at the view that the special characters which are expressed by the word *acid* are not necessarily connected with the presence of any one element,[1] that most acids are compounds of hydrogen with certain elements or groups of elements, and that salts are compounds of metals with the elements which combine with hydrogen to form acids.

By tracing the history of the elucidation of the compositions of muriatic acid and oxymuriatic acid gas, I have shown how dexterously that view of the compositions of acids and salts which had seized the imaginations of chemists was made to cover the facts established in the laboratory. Davy made his experiments quantitative, he compared one set of quantitative results with other series of quantitative results, and he adopted

---

[1] "When certain properties are found belonging to a compound, we have no right to attribute these properties to any of its elements to the exclusion of the rest, but they must be regarded as a result of combination."

"It is impossible to infer what will be the qualities of a compound from the qualities of its constituents."—Sir H. Davy "On the analogies between the undecomposed substances, and on the constitution of acids." *Quart. J. of Science*, **1**, p. 283 [1816].

without reserve the definition of an element established by Lavoisier—a substance which has not been decomposed. Chemists were forced to admit that the theory which had guided their attempts to discover the nature of acids and of salts had done its work and required profound modification.

Both those who upheld the older view of the constitution of acids, and those who said that view was insufficient to cover the facts, used analogy as the main guide in their experimental work. The history of muriatic acid and oxymuriatic acid gas shows that chemical analogy is a dangerous guide unless it is finely handled.

The newer notions concerning acids and salts made way slowly; many years passed before they were stated as exact generalizations. The work of Gay-Lussac on hydriodic and prussic acids, and salts of these acids, taken with the establishment of the compositions of muriatic acid and its salts, led to the division of acids into two classes; hydracids and their salts were contrasted with oxyacids and their salts. As only a few hydracids were known, attention was given for many years, from 1815 onwards, to the establishment of analogies between oxyacids and the salts of these acids. The view continued to hold the field that both these classes of compounds are compounds of "anhydrous acids" with bases; the acids were considered to be compounds of anhydrous acids with basic water, the salts were regarded as compounds of anhydrous acids with alkalis, earths, or metallic calces.

In 1833, Graham published the results of an important research on *Arseniates, phosphates, and modifications of phosphoric acid.*[1] The composition of the compound which was then called phosphoric acid was expressed by the formula PO_5. Graham proved the existence of three "acid hydrates," to which he gave the compositions[2] $PO_5.3HO$, $PO_5.2HO$, and $PO_5.HO$. He regarded these as terphosphate of water, biphosphate of water, and phosphate of water; he thought of them as modifications of phosphoric acid, distinguished from one another by "the quantity of water combined with the acid."

---

[1] *Phil. Trans.* for 1833, p. 253.
[2] Graham took the atomic weight of oxygen to be 8.

He said that one of the three atoms of water in the first hydrate could be replaced by one atom of soda, two atoms of water by two atoms of soda, and three atoms of water by three atoms of soda; that half or the whole of the water in the second hydrate could be replaced by one or by two atoms of soda; and that the water in the third hydrate could be replaced by one atom of soda. He thus distinguished three classes of phosphates; those formed of one atom of phosphoric acid (PO_5) and three of base, for he regarded the water in the hydrates as basic water, those formed of one atom of phosphoric acid and two atoms of base, and those formed of one atom of phosphoric acid and one atom of base. Graham said, in effect; when the salt $PO_5.NaO.HO$ is heated it loses water and becomes the salt $PO_5.NaO$, when the salt $PO_5.HO.2NaO$ is heated it loses water and becomes the salt $PO_5.2NaO$, and the salt $PO_5.3NaO$ is produced by completely neutralizing the hydrate $PO_5.3HO$ by soda. Graham concluded that all the salts *contained* one atom of phosphoric acid (PO_5); one series *contained* three atoms of base, another series *contained* two atoms of base, and the third series *contained* one atom of base.

In 1838, Liebig endeavoured to determine the constitutions of a number of acids, composed of carbon, hydrogen, and oxygen, by examining the products of their decomposition under different conditions.[1] Liebig began by attempting to represent the various salts which he examined, as Graham had represented the phosphates, as compounds of anhydrous acids and bases, water being regarded as a base. He found that this led to results which were opposed to the fundamental assumption that all salts of an oxyacid must contain that acid and a base. For instance, Liebig's analyses of tartar emetic dried at 250° were expressed by the formula $C_8H_8O_{10}.KO.Sb_2O_3$; when this salt[2] was heated to 300° it lost "two atoms" of water, and became $C_8H_4O_8.KO,Sb_2O_3$; but, Liebig argued, the salt dried at 250° could not *contain water as such,* and therefore it was necessary to represent the two salts as containing different acids, although

_____

[1] *Ueber die Constitution der organischen Saüren. Annal. Chem. Pharm.*, **26,** 113 [1838].
[2] The atomic weights used by Liebig were (approximately) these: $O = 16$, $C = 12$, $K = 78$, $Sb = 120$.

both were salts of tartaric acid. Liebig then examined the argument, on which rested most of the formulæ given to the salts of oxyacids, that because a compound yields such and such substances when it is decomposed, therefore it contains these substances. He found that the products of decomposition of the acids, and of the salts he was examining, were different under different conditions. Under certain conditions the acid X decomposed into the compounds A, B, C; therefore, the argument ran, X contains A, B, C. But under other conditions the same acid decomposed into the compounds a, b, c; therefore, if the reasoning is good, X contains a, b, c. Referring to different decompositions of the same organic compound which led to two different views of the constitution of that compound, Liebig said:

> " The two views are merely expedients employed by the mind to give an account of certain phenomena, and to bring these into relation with one another; and all views of the constitution of chemical compounds are to be thought of in no other way but this. A theory is the elucidation of positive facts which do not allow us to draw undeniable conclusions concerning the constitution of a substance from its behaviour in different processes of decomposition, because the products vary according to the conditions of the decomposition. Every view of the constitution of a substance is true for certain cases, but it is unsatisfactory and insufficient for other cases. . . . We are agreed to call the *chemical properties* of a substance those phenomena, that behaviour, which it exhibits when it interacts with other substances; now, the behaviour of organic substances has enabled us to assert positively that chemical properties vary according to the materials which react with the substance under examination. These properties are, therefore, not absolute; they are not inherent in the substance. Every theory which is based on processes of decomposition is incomplete and insufficient."

Liebig used these generalizations from experience as guides in examining the consistency, comprehensiveness, and direct applicability to the facts as a whole, of the two hypotheses regarding the constitution of acids. Taking as his first example sulphuric acid and potassium sulphate, he described the constitutions of these compounds in terms of the two views.

What might be called the orthodox view in 1838 said that sulphuric acid has the composition SO_3, that this acid combines with potassium oxide, KO, and the product is sulphate of potash, $SO_3.KO$ (K = 78, O = 16, S = 32). It was admitted that sulphuric acid combines with water; the compound, $SO_3.H_2O$,

was called a hydrate of sulphuric acid. The view which was adumbrated by Davy about 1815 (and also by Dulong) said that sulphuric acid is a compound of hydrogen, it has the composition H_2SO_4 (using Liebig's atomic weights), and is comparable in composition with the hydracid H_2S; potassium sulphate is KSO_4 ($K = 78$).

If it can be certainly proved, Liebig said, that sulphate of potash contains sulphuric acid (SO_3) and potash (KO), there is an end of Davy's hypothesis; but no conclusive proof has been given, or can be given of this assertion. Take potassium chloride and potassium cyanide, Liebig said; there is no doubt that one is KCl and the other is KCN. But turn to sulphocyanide of potash: it may be a compound of sulphide of cyanogen and sulphide of potash, or it may be a compound of potassium, sulphur, and cyanogen; the first hypothesis represents it by the formula $Cy_2S.SK$, and to the corresponding acid it assigns the composition $Cy_2S.SH_2$; the second hypothesis gives the formulæ Cy_2S_2K, and Cy_2S_2H to the salt, and its corresponding acid ($K = 78$). The first hypothesis makes sulphocyanide of potash comparable with the salts of oxyacids, but puts it in a different class from the salts of hydracids, KCl and KCN for instance. The second hypothesis gives similar constitutions to potassium sulphate, potassium sulphocyanide, potassium chloride, and potassium cyanide, and, indeed, to all neutral salts. The chief argument in favour of the ordinary view is that potassium and oxygen, and potassium and sulphur, readily combine, and that potassium oxide and sulphuric acid (SO_3) readily combine; therefore, it is argued, sulphate of potash very probably contains potassium oxide, and sulphocyanide of potash very probably contains sulphide of potash.

What we certainly know, Liebig said, is that base + acid = salt + water. When lime and sulphuric acid react, sulphate of lime and water are produced; when lime and hydrochloric acid react, chloride of lime and water are produced. The hypothesis which asserts a difference of kind between the salts of oxyacids and the salts of hydracids says that water is in sulphuric acid before the reaction begins between lime and that acid, but that in the reaction between hydrochloric acid and lime water is

formed by the union of the hydrogen of the acid with oxygen of the base. Davy's hypothesis says that the two reactions are strictly similar; that in both the metal of lime replaces the hydrogen of the acid, and this hydrogen combines with the oxygen of the lime to form water.

Liebig decided in favour of the view which brings the reactions of all acids with bases under a common scheme. See, he said, how admirably the view of Davy represents the acids of chlorine:

$$
\begin{array}{lll}
\text{Hydrochloric acid} & \text{``} & Cl_2 + H_2 \\
\text{Hypochlorous} & \text{``} & Cl_2O_2 + H_2 \\
\text{Chlorous} & \text{``} & Cl_2O_4 + H_2 \\
\text{Chloric} & \text{``} & Cl_2O_6 + H_2 \\
\text{Perchloric} & \text{``} & Cl_2O_8 + H_2.
\end{array}
$$

Liebig declared acids to be certain compounds of hydrogen, the hydrogen of which can be replaced by metals; neutral salts, he said, all belong to one class, they are the compounds which are formed by replacing the hydrogen of acids by equivalent quantities of metals. The saturation-capacity of an acid is dependent on the quantity of hydrogen in it, or on the quantity of replaceable hydrogen in it. If we use the expression "radical of an acid" to mean the acid except its replaceable hydrogen, then we have the formula *radical + replaceable hydrogen* as an expression of the compositions of all acids. We have many examples of acids, especially organic acids, whose saturation-capacities are the same although the compositions of their radicals are different.

Liebig expressed the compositions of the three phosphoric acids, and the relations between them, by the formulæ

$$
\begin{array}{ll}
P_2O_8 + H_6 & \text{phosphoric acid} \\
P_2O_7 + H_4 & \text{pyrophosphoric acid} \\
P_2O_6 + H_2 & \text{metaphosphoric acid.}
\end{array}
$$

The view of the constitution of acids, and the relations between their compositions and those of their neutral, or normal salts, which Liebig clearly enunciated in 1838, has been found to cover the facts. It has been amplified and refined, but not essentially changed.

In 1839 and 1840, Daniell showed that many salts separate into two parts when an electric current is passed through their aqueous solutions, the two parts being a cation, which is the metal of the salt, and an anion, which is what Liebig called the radical of the salt. In a series of memoirs, published from 1853 to 1859, Hittorf extended the work begun by Daniell, and expressed his results in the general statement: *acids, bases, and salts are electrolytes;* in other words, aqueous solutions of these compounds conduct the electric current and are thereby themselves decomposed.

The later developments of the electrolytic theory of acids, bases, and salts will be described in the chapter which deals with the history of the hypothesis of the ionization of salts in dilute solutions. (Chapter XII.)

The development of the view that acids are compounds of hydrogen and different radicals, and salts are compounds of metals and radicals, is intimately connected with that general conception of salts, and compounds allied to salts, which was called *the unitary hypothesis*, and will be better understood when I am tracing the history of that hypothesis in Chapter IX.

The chemical histories of the three classes of compounds, acids, salts, and bases, are closely interwoven. We have seen (pp. 203-207) that Black's quantitative experiments led to the division of alkalis and earths into two classes; mild alkalis and mild earths, and caustic alkalis and caustic earths or quick-limes. We have seen that at about the time of the discovery of oxygen, salts were thought of as compounds formed by the addition of acids to bases which were generally alkalis or earths; if a mild alkali or a mild earth was the basis, fixed air escaped; if a caustic alkali or earth was the basis, fixed air was not produced. Besides being built on the bases of alkalis and earths, salts could be formed by adding acids to the calces of metals. When Lavoisier had proved calces to be oxides, the theory of the composition of acids and salts was almost complete. Analogy indicated that the alkalis and the earths must be oxides of metals. If experimental investigation should confirm this supposition, the edifice was finished.

Let us briefly trace some of the steps in the history of the demonstration of the nature of alkalis and of earths.

Substances which had detergent properties, dissolved oils and sulphur, were used in making glass, and changed the colours of green plants, were classed together many centuries ago under the common name *alkali* (from the Arabic = the ash); because the substances were obtained by calcining various materials and reducing them to ashes. Three kinds of alkali were spoken of in the eighteenth century and during part of the nineteenth; *vegetable alkali* now called potash, *mineral alkali* now called soda, and *volatile alkali* now called ammonia. The name *earths* was given to substances which more or less resembled alkali. Lavoisier asserted the alkalis to be compounds of oxygen, " although," he said, "we do not yet know the nature of the principles which enter into their composition." He thought it likely that the earths would be proved to be oxides of metals.

Early in the nineteenth century Davy turned his attention to the decompositions effected by electricity. In 1807 he proved that hydrogen and oxygen are the sole components of water. In 1808, the year in which Dalton's *New System of Chemical Philosophy* appeared, Davy published a memoir on the decomposition of the fixed alkalis by electricity.[1] After describing the Voltaic pile which he used, Davy said:

"A small piece of pure potash was placed upon an insulated disk of platina, connected with the negative side of the battery, . . . and a platina wire communicating with the positive side was brought into contact with the surface of the alkali. The potash began to fuse at both its points of electrization. There was a violent effervescence at the upper surface; at the lower, or negative, surface, there was no liberation of elastic fluid; but small globules, having a high metallic lustre, and being precisely similar in visible characters to quicksilver, appeared, some of which burnt with explosion and bright flame, as soon as they were formed, and others remained, and were merely tarnished, and finally covered with a white film which formed on their surfaces."

Soda behaved similarly to potash.

Davy had expected to obtain oxygen at the positive pole; he proved the gas which came off with "violent effervescence " to be oxygen. He then burnt in oxygen the new metal-like

[1] *Phil. Trans.* for 1808, p. 1, *On some new phenomena of chemical changes produced by electricity, particularly the decomposition of the fixed alkalis* . .

substances obtained from potash and soda, and proved the products to be potash and soda.

Davy concluded that the new substances were "peculiar inflammable principles the bases of potash and soda." He burnt weighed quantities of the two substances in oxygen, weighed the products, and measured the oxygen absorbed; he also caused amalgams of the two "peculiar inflammable principles" to react with water, and measured the hydrogen which was produced. He concluded that "100 parts of potash consist of about 84 basis and 16 oxygene." [1]

Davy's experiments led him to place the two new bases in the class of metals. He showed them to various friends, whom he asked whether they thought these substances were metals. "The greater number of philosophical persons to whom this question has been put have answered in the affirmative." As Davy agreed with the "philosophical persons," he named the new substances *potassium* and *sodium*. These names, he said, merely declare the substances to be "the metals produced from potash and soda"; the names will remain, however chemical theories may change.

In the same year, 1808, Davy used electricity to decompose the four earths, baryta, lime, strontia, and magnesia.[2] He passed the current through mixtures of the earths and red oxide of mercury. After hearing from Berzelius that he had obtained amalgams of the metals of baryta and lime, by passing the electric current through these earths in contact with mercury, Davy used mercury in place of its oxide. He removed the mercury from the amalgams by distillation, and although he did not obtain pure specimens of the bases of the earths, he conclusively proved these bases to be metals. He called the new metals *barium, calcium, strontium,* and *magnium;* the last name being used because *magnesium* had been "already applied to metallic manganese." [3]

---

[1] Potassium oxide, K_2O, is composed of almost 83 per cent. potassium and a very little more than 17 per cent. oxygen.
for 1808, p. 333.

[2] *Electrochemical researches on the decomposition of the earths,*   *Phil. Trans.*

[3] A black mineral had long been known under the name *magnesia nigra.* A new medicine was introduced in the early years of the eighteenth century, and was called *magnesia alba.* After a time *magnesia nigra* came to be known by the

Davy then tried to decompose the earths alumina, glucina, silica, and zirconia, but he did not succeed.[1]

Davy now turned his attention to "the nature of ammonia and alkaline bodies in general."[2] The composition of ammonia had been considered by Scheele, Priestley, and especially by Berthollet. The last named naturalist concluded from his experiments that ammonia is a compound of nitrogen and hydrogen, and that three volumes of hydrogen combine with one volume of nitrogen to form two volumes of ammonia.[3] Davy argued that the compositions of potash, soda, and ammonia are probably similar, because all of them are alkaline substances. Potash and soda are composed of metal and oxygen; therefore, ammonia may contain oxygen. "Of the existence of oxygene in volatile alkali," Davy says, "I soon satisfied myself." Purified charcoal was burnt in dried ammonia, the charcoal being heated by an electric current; a great expansion of the gas was noticed, and a white substance was deposited which effervesced with acids, and was probably carbonate of ammonia. Some water was obtained by passing dried ammonia over heated iron wire, and the iron became coated with oxide. Davy says he took care to prove that the ammonia he used did not contain water. He collected four tenths of a grain of water, and obtained a mixture of nitrogen and hydrogen in the ratio of about 74 volumes of hydrogen to 26 volumes of nitrogen. Measurements of the products of the decomposition of ammonia by electricity gave varying results; on the whole, the total weight of the mixed gases obtained was rather less than the weight of the ammonia used. This result, Davy said, "can only be ascribed to the existence of oxygene in the alkali, part of which

name *manganese.* A metal was obtained from manganese in the eighties of the eighteenth century by Gahn. The metal was at first called *magnesium;* then, to avoid confusion between the name and *magnesia alba,* the name of the new metal was changed to *manganesium;* finally, some time after Davy's isolation of the metal of *magnesia alba,* the name *manganese* was used for the metal of *magnesia nigra,* and the metal of *magnesia alba* was called *magnesium.* Many beginners in chemistry perpetuate the ancient confusion in the nomenclature of the two metals.

[1] Alumina was decomposed by Wöhler in 1828; glucina by Wöhler in 1827, silica by Berzelius in 1823, and zirconia by Berzelius in 1825. The bases of alumina, glucina (beryllia), and zirconia were found to be metals; silica was proved to be the oxide of a non-metallic element.

[2] *Phil. Trans.* for 1808, p. 353.

[3] *Journal de Physique* for 1785, vol. ii. p. 176.

probably combined with the platina wire employed for electrization, and part with hydrogene.''

The general conclusion reached by Davy at this time (1808) regarding the alkali was expressed by him thus:

"Oxygene then may be considered as existing in, and as forming an element in all the true alkalies; and the principle of acidity of the French nomenclature might now likewise be called the principle of alkalescence."

Davy repeated the experiment described by Berzelius of negatively electrifying mercury in contact with a solution of ammonia, and confirmed the assertion of Berzelius that a substance of the nature of an amalgam is formed. Davy agreed with the conclusion which Berzelius had drawn from his experiments that the amalgam is composed of the "deoxygenated basis of ammonia, and mercury," and that this basis is a metal. But, although the deoxygenated basis of ammonia was thought by Davy to be a metal, he had to acknowledge that it was almost certainly composed of nitrogen and hydrogen. "Are nitrogen and hydrogen really metals in an aeriform state," he said, or are they "oxides which become metallized by deoxidation?" Perhaps, he suggested, they may be "simple bodies, not metallic in their own nature, but capable of composing a metal in their deoxygenated, and an alkali in their oxygenated state." The experiments which Davy made in 1809 on the action of ammonia on potassium strengthened his view that nitrogen is a compound of oxygen with some other substance or substances.[1]

In 1810 he returned to the subject of the nature of nitrogen;[2] the results of his experiments were inconclusive. He could not decide the exact composition of ammonia. His own experiments gave the mean result that 73·74 volumes of hydrogen are combined with 26·26 volumes of nitrogen; he still thought that ammonia contained about one eleventh or one twelfth of its weight of oxygen and water. Henry attempted to determine the composition of ammonia in 1809, by decomposing the gas by electricity.[3] He obtained almost 199 volumes of nitrogen and hydrogen from 100 volumes of ammonia, and confirmed

Davy's result that the two gases were present in the mixture approximately in the ratio of 74 volumes of hydrogen to 26 volumes of nitrogen.

In their *Recherches Physico-chimiques*, published in 1811, Gay-Lussac and Thenard [1] examined the amalgam formed by electrifying ammonia in presence of mercury, proved that it gave off ammonia and hydrogen under conditions which ensured the absence of water, and concluded it to be composed of mercury, ammonia, and hydrogen, and not, as Berzelius and Davy supposed, of mercury and the "deoxygenated basis of ammonia." They also concluded that ammonia does not contain oxygen, and is a compound of nitrogen and hydrogen, which substances they classed as elements. As, according to their view, ammonia combines with hydrogen to form a metal-like substance which produces an amalgam similar to potassium amalgam, Gay-Lussac and Thenard started the hypothesis that Davy's metal potassium is really a compound of hydrogen with an unknown basis. This hypothesis was shown by Davy to be without any foundation of facts; [2] but it introduced more complexity into the subject of the compositions of the alkalis.

In his *Elements of Chemical Philosophy*, published in 1812, Davy placed nitrogen among the undecompounded substances; he described ammonia as a compound of nitrogen and hydrogen; but he could not decide the nature of the amalgam from ammonia (or ammonium amalgam, as it was generally called at that time). He still thought it possible that nitrogen might be an oxide of a peculiar metal, and hydrogen another oxide of the same peculiar metal, which is the basis of ammonia.

In the first German edition of his *Lehrbuch*, published in 1825, Berzelius was inclined to regard nitrogen as the oxide of a "peculiar inflammable radical," which he provisionally named *nitricum*. Arguing from the analogies between ammonia, potash, and soda, Berzelius said that in the amalgam from ammonia "there must be a metallic substance combined with the mercury, and this metal we call ammonium." Berzelius brought the formation of a salt, by the action of an aqueous solution of ammonia on an acid, within his general scheme of the

[1] *Recherches*, vol. i. pp. 52–73.   [2] *Phil. Trans.* for 1810, p. 16.

formation of salts, by supposing that ammonia, composed of nitrogen and hydrogen, decomposed part of the water, and combined with the hydrogen to form the compound metal ammonium, which was oxidized by the oxygen of the water, and that the oxide of ammonium then combined with the acid if an oxyacid was used, or with the salt-forming part of the acid if a hydracid was employed. This view was more fully developed by Berzelius in the fifth edition of his *Lehrbuch* (1843).[1] He says that ammonium is "a compound radical which possesses all the properties of an alkali metal"; that in the salts of ammonium the nitrogen and hydrogen which compose it are held firmly together, but ammonium oxide and ammonium hydrate are easily separated into ammonia and water. The oxide, he says, is known only in combination with electronegative substances. The formation of ammonium amalgam is cited by him as a convincing proof of the ammonium hypothesis.

In 1839 and 1840, in the course of experiments on the electrolysis of salts, Daniell showed that the simplest presentation of the facts concerning ammonium salts was to regard these compounds as containing the cation NH_4, analogous to the cations K and Na. Later electrolytic investigations have brought out the resemblances between potash, soda, and ammonia, in aqueous solutions, by representing them all as containing univalent cations (K, Na, NH_4), and univalent anions OH. The history of these developments of the views of Davy and of Berzelius will be considered in Chapter XII.

The division of certain compounds into the classes of acids, bases, and salts carried with it the possibility of placing many of the oxides in one or other of two classes, namely, basic oxides and acidic oxides. And this classification went hand in hand with that which placed many of the elements together under the designation of acid-forming elements, and many others under that of base-forming elements. The names metal and non-metal were often taken as synonymous, or nearly synonymous with the terms base-forming element and acid-forming element; and these terms were nearly interchangeable with the others, electropositive and electronegative element. Classifications

based on the differences between electropositive and electro-
negative elements played a very important part in the doctrine
of electro-dualism, which was promulgated by Berzelius, and
prevailed for many years in chemistry. The history of this
phase of the classification of homogeneous substances will be
considered in the next chapter.

The history of the development of the terms acid, base, and
salt furnishes examples of the tyranny of phrases. Scheele
called the new gas he discovered *dephlogisticated marine acid,*
and for many years every one who examined this gas assumed
it to be an acid. Lavoisier demonstrated the importance of
Priestley's dephlogisticated air in chemical changes of many
kinds; in the word *oxygen* he perpetuated his view that this
element is *the* acid former. The labours of a vast number of
chemists during more than half a century were required to
prove that Lavoisier had drawn a boundary-line which does not
exist in nature.

Over the history of chemistry is written *choose your words
and expressions carefully.* We are describing the relations of
facts—mere cataloguing is not science—the expressions we use
embody those views of these relations which hold the field at
present; the true relations are discovered very slowly, and the
course of their discovery is being constantly distorted by ex-
pressions which assume the present views to be final.

CHAPTER IX.

RADICALS, TYPES, DUALISM, AND THE UNITARY HYPOTHESIS.

In the last chapter we considered the history of the division of certain compounds into the classes of acids, bases, and salts, a division which carries with it the distinction between acidic and basic oxides, and that between acid-forming and base-forming elements.

We saw that in his investigation of prussic acid in 1815, Gay-Lussac isolated cyanogen, and spoke of that substance as "a remarkable example, and at present a unique example, of a body which although a compound plays the part of a simple body in its combinations with hydrogen and with the metals." We saw the introduction into chemistry, by Berzelius, of the "compound radical ammonium which possesses all the properties of an alkali metal." We have now to trace some of the effects of the hypothesis of compound radicals on the development of the classification of compounds. The compound radical of the earlier chemists was a successor of the alchemical "principle" or "element." Lavoisier gave definiteness to the conception, and made it directly applicable to particular cases of chemical change, by presenting a list of the radicals of various acids, which, he said, "enter into combination after the manner of simple substances." [1] The strength of the hold on the minds of those who came after him, of Lavoisier's view of the constitution of acids and of salts, is shown by the pertinacity wherewith they clung to the notion that an unknown radical enters into the composition of muriatic acid, in spite of the many failures to

---

[1] *Œuvres*, vol. i. p. 138.

obtain from that compound the radical whereof it was declared to be an oxide.

Gay-Lussac's isolation of cyanogen, in 1815, was followed by the publication of various memoirs wherein particular compounds, most of them organic compounds, were considered to be formed by the union of two or more radicals. It looked as if organic compounds would come to be described as collocations of compound radicals. Ten years after Gay-Lussac had isolated cyanogen, Faraday [1] prepared a compound of carbon and hydrogen from liquefied coal-gas, determined the composition of one volume of the gaseous compound to be C_4H_4, compared the reactions of the compound with those of olefiant gas, the composition of one volume of which he expressed by the formula C_2H_2, and thus started chemists on the study of the phenomena now called isomerism.[2] The only way which could lead to the classification of the relations of organic compounds appeared to be that which should begin with the study of the radicals of these compounds; for, if two compounds have the same elementary composition and the same density in the state of gas, and differ in their reactions, these differences must surely be associated with differences between the modes of arrangement of the elements of the compounds, in other words, with the existence of different radicals, different groups of elements, in the compounds.

The hypothesis that the reactions of many organic compounds are the reactions of the radicals, or compounded elements, whereof they are supposed to be constituted, was greatly advanced, and brought prominently into the daily mental lives of chemists, by the researches on the radical of benzoic acid, by Wöhler and Liebig, published in 1832.[3] Wöhler and Liebig prepared a series of compounds from oil of bitter almonds, and studied the relations of these compounds by examining their reactions of formation and decomposition. After describing the compounds and their reactions, Wöhler and Liebig said:

[1] *Phil. Trans.* for 1825, p. 440.
[2] The history of isomerism will be considered in Chapter XI.
[3] "Untersuchungen über das Radikal der Benzoesäure," *Annal. Chem. Pharm.*, **3**, p. 249 [1832].

"When we look over and epitomize the phenomena which are described in the foregoing communication, we find that they all group themselves round a single compound which is unchanged in its nature and composition in almost all of its reactions of combination with other substances. This stability induced us to regard that substance as a compounded element, and to propose for it a special name, the name *benzoyl*.[1] We have expressed the composition of this radical by the formula $14C + 10H + 2O$. Benzoyl combines with one atom of oxygen to form anhydrous benzoic acid, and with one atom of oxygen and one atom of water to form crystallized benzoic acid. With two atoms of hydrogen it forms pure oil of bitter almonds; when this changes to crystallized benzoic acid by standing in the air, it takes up two atoms of oxygen, one of which produces benzoic acid by combining with the radical, and the other combines with two atoms of hydrogen and produces the water of the crystallized acid. Moreover, the place of the hydrogen in the oil, or of the oxygen in the benzoic acid, can be taken by chlorine, bromine, iodine, sulphur, and cyanogen; and all the compounds which are thus produced, and also the corresponding phosphorus compounds, are decomposed by water with formation of benzoic acid and a hydrogen acid.

The replacement of two atoms of hydrogen in the pure oil by the halogens seems to us a decisive proof in favour of the supposition that there is a special kind of combination between this hydrogen and the other elements; this special kind of combination is rather indicated than sharply defined by the notion of the radical, borrowed from inorganic chemistry. . . . We think it is not unlikely that there may be several groups of organic bodies . . . which are built on the foundation of the same radical acting as a compounded element."

Wöhler and Liebig sent a copy of their memoir to Berzelius. In acknowledging it, Berzelius said:

"The results you have drawn from the investigations of the oil of bitter almonds are certainly the most important which have hitherto been obtained in the domain of vegetable chemistry, and promise to spread an unexpected light over this branch of science. The fact that a substance which is composed of carbon, hydrogen and oxygen combines with others, after the manner of a simple substance, and especially with salt-forming and with base-forming substances, decides that it is a ternary compound atom (of the first order); and the radical of benzoic acid is the first definite example of a ternary substance which possesses the properties of a simple substance. The facts you have brought to light suggest so many speculations, that one may indeed regard them as the beginning of a new day for vegetable chemistry. I would suggest that that substance which is the first example of a compound radical composed of more than two bodies should be called *Proin* (from πρωί, the beginning of the day) or *Orthrin* (from ὄρθρός, daybreak)."

It is interesting and instructive to know that a few years after Berzelius rejoiced at the coming of the day, he cast forth *proin*,

---

[1] The termination of this name is derived from the Greek ὕλη=stuff or matter.

orthrin, or *benzoyl* from the class of radicals, declaring "an oxide cannot be a radical,"[1] and "ternary radicals are either compounds of a binary substance with a simple substance, or they are compounds of two binary substances."[2]

Berzelius also said:

"From the moment when one has learnt to recognize with certainty the existence of ternary atoms of the first order which enter compounds after the manner of simple substances, it will be a great relief in the expression of the language of formulæ to denote each radical by its own symbol, whereby the idea of composition it is desired to express will be placed clearly before the eye of the reader."

Berzelius illustrated his proposal by the following formulæ, wherein $B_z = C_{14}H_{10}O_2$. $B_zO =$ benzoic acid; $B_zH_2 =$ oil of bitter almonds; $B_zCl_2 =$ chlorbenzoyl, $B_zS =$ benzoyl sulphide; $B_z + NH_2 =$ benzamide.

Speaking of their representation of several similar substances as compounds of one and the same group of three elements, Wöhler and Liebig said:

"The only guide which led us to this view has been the series of closely allied phenomena we have observed. A man with a pen in his hand, ready to make calculations, and arbitrary changes in the analyses which others have made of organic compounds, can easily discover many similar radicals; but we think that science is very little served by raising expectations which rest on no adequate basis of facts."

After suggesting formulæ for several series of compounds, each series being represented as compounds of the same radical, Berzelius finished his letter to Wöhler and Liebig by saying:

"I must insist that such formulæ should be received only when the ideas which they ought to express have some claim to be acknowledged as proved facts, otherwise they can but lead to confusion like that of Babel."

As we proceed, we shall see that the advice of Wöhler and Liebig and the warning words of Berzelius were soon forgotten.

Berzelius spoke of benzoyl as "a compound ternary atom of the first order." This expression was a phrase of the language wherein Berzelius expressed his doctrine of electrodualism.

In the first of a series of memoirs in the *Philosophical Transactions* on the chemical decompositions effected by electricity,

---

[1] *Jahresbericht* for 1839, p. 358.   [2] *Annal. Chem. Pharm.*, **31**, 13 [1839].

Davy,[1] in 1807, tried to connect positive and negative electricity with the chemical affinities of substances. "May not the electrical energy," he said, "be identical with chemical affinity and an essential property of matter?" Davy supposed that chemical union always occurs between differently electrified substances.

"Suppose two bodies, the particles of which are in different electrical states, and those states sufficiently exalted to give them an attractive force superior to the power of aggregation, a combination would take place which would be more or less intense according as the energies were more or less perfectly balanced, and the change of properties would be correspondingly proportional."

If two substances with different degrees of the same electrical attracting energy acted on one another, Davy supposed that combination would be determined by the degree, "and the substance possessing the weakest energy would be repelled." "This principle would afford an expression of the causes of elective affinity, and the decompositions produced in consequence." Berzelius adopted Davy's suggestions, developed them, and founded on that development the system of dualism which reigned supreme for many years. I propose to give an analysis of parts of the memoir wherein Berzelius laid the foundations of his system.[2]

Berzelius stated his doctrine of dualism in the language of the atomic theory. He spoke of compound atoms of various orders of complexity. Compound atoms of the first order are formed, he said, by the union of elementary atoms, inorganic compounds by the union of the atoms of two elements, most ogranic compounds by the union of atoms of at least three elements. Compound atoms of the second order are formed by the union of atoms of the first order; an atom of sulphate of potash is formed by the combination of an atom of sulphuric acid and an atom of potash, sulphate of alumina by the com-

---

[1] *Phil. Trans.* for 1807, p. 2.

[2] *Versuch einer theoretischen Ansicht von den Chemischen Proportionen und dem Chemischen Einflusse der Elektricität in der unorganischen Natur.* Berzelius: *Lehrbuch der Chemie*, First German Edition [1825] vol. iii, Part I, pp. 16–131; especially "Entwickelung der electrochemischen Theorie," pp. 49–87. The account in the text is a free and much condensed translation of the words of Berzelius.

bination of three atoms of sulphuric acid and one atom of alumina. Compound atoms of the third order are formed by the union of atoms of the second order; dry alum, for instance, is formed by the union of an atom of sulphate of alumina with an atom of sulphate of potash. Hydrated alum, formed by the combination of an atom of alum with several atoms of water, is classed by Berzelius as a compound atom of the fourth order. Berzelius held that "neutralization of the opposite electricities happens whenever a chemical compound is formed." If the constituents of a compound are held together by a special force inherent in the atom, then the continuance of combination must be independent of electrical conditions. If the close union is caused by some property of electricity, then the restoration of the electrical polarity of the constituents must be accompanied by the breaking-up of even the most stable compounds. We know that compounds are decomposed by electricity. This shows that what we call chemical affinity is necessarily and intimately connected with electrochemical phenomena.

Substances are either electropositive or negative:

"The simple substances which belong to the first class, and also their oxides, are always electropositive when brought into contact with simple substances, or oxides, belonging to the second class; and oxides of the first class always behave towards oxides of the second class as the bases of salts behave towards acids."

"An electrochemical system is obtained by arranging substances in accordance with their electrical properties, and this system is better suited than any other for giving a general idea of chemistry."

Oxygen is the most electronegative of all substances; it is never positive relatively to another substance. "Oxygen is the only substance in the electrochemical system whose electrical relations are unchangeable." Each of the other substances is electropositive to some and negative to some other substances. "The radicals of the fixed alkalis, and of the alkaline earths, are the most electropositive substances." But "no substance is so electropositive as oxygen is electronegative."

Berzelius then gives a list of elements arranged in electrical order, beginning with the most electronegative, oxygen, and finishing with the most electropositive, sodium and potassium. He notes that the arrangement is to be regarded as only ap-

proximately accurate. He divides the oxides into acids, which are electronegative, and bases, which are positive. He says that a weak acid sometimes acts as a base towards a stronger acid, and a weak base sometimes plays the part of an acid towards a stronger base.

Salts, which are composed of an acid and a base, react one with another in two ways: there may be a decomposing action whereby the elements combine in other proportions; and there may be a uniting action, whereby two salts form a double salt wherein one is electropositive and the other is electronegative. The decomposing action is conditioned by the specific electrical reactions of the individual elements which strive towards more complete neutralization; the combining action is connected with the electrical reaction of the compound atoms which strive, as wholes, towards more complete electrical neutralization. Although there is no absolute electrical indifference some compounds are nearly electrically indifferent. This approximate indifference is caused by the almost complete electrical neutralization of the compounds as wholes; nevertheless the elements of these compounds retain their specific reactions towards substances which strive to decompose the compounds. Crystallized alum, for instance, will not combine with other substances, but it is decomposed by many.

Because of lack of facts, Berzelius said he could only attempt a theoretical answer to the question, How does electricity exist in substances? How is a substance electropositive or negative? A substance is not electrical, he said, without manifesting both electricities, either in different parts of itself or in its sphere of action. If the electricities are manifested in a substance which is continuous, they are always concentrated in two opposing points, and the electric condition of the substance has the same polarity as a magnetic body. Every smallest part of an elementary substance must be thought of as having the properties of the whole, therefore every smallest part must show polarity. Adopting the language of the atomic theory, every atom of a substance must possess electric polarity; the electrochemical phenomena which are manifested when the atoms combine depend on their polarities; and the unequal intensities of

the polarities of the atoms is the cause of the differences between their affinities.

This electric polarity of the smallest particles of substances does not suffice to explain the specifically positive electricity of certain substances and the specifically negative electricity of others. This property probably depends on a kind of electrical one-sidedness (*Einseitigkeit*), which has been called *unipolarity*, and is not yet understood. One pole of a magnet may be much stronger than the other: so we may suppose the electricity of one pole of an atom to be predominant, or concentrated, at a certain point; we may suppose the positive pole of one substance, and the negative pole of another, to predominate, because each smallest particle has a specific unipolarity.

This hypothesis helps us to understand how electricity is present in substances, and wherein their electrochemical properties consist.

Substances are electropositive or negative as one or the other pole predominates. Specific unipolarity does not explain all the phenomena; for instance, sulphur and oxygen, both of which are electronegative, combine much more intimately than copper and oxygen, although copper is electropositive. The degree of affinity of a substance does not depend on its specific unipolarity, but it must generally be deducible from the intensity of its polarity. Certain substances are capable of a more intense polarization than others; they must, therefore, have a greater tendency to neutralize the electricity distributed on their poles, that is, they must have a greater affinity than the other substances. Although the unipolarities of sulphur and oxygen are the same, nevertheless the positive pole of sulphur neutralizes more negative electricity on the predominant pole of oxygen than can be neutralized by a metal, say by lead. Specific unipolarity must be clearly distinguished from intensity of polarization.

The electrochemical properties of most oxidized compounds depend entirely on the unipolarities of their more electropositive elements, that is, of their radicals. If the radical of one oxide is electronegative to the radical of another, the first oxide is negative to the second, and the converse is true. Sulphuric

acid is negative towards all metallic oxides, because sulphur is negative to all metals. The oxides of potassium and zinc are electropositive to all oxides towards the radicals of which potassium and zinc are positive. This fact serves to correct an erroneous idea about the acidifying principle, oxygen. The acidity of an acid is dependent on the radical of the acid: oxygen plays an indifferent part, for it enters into the compositions both of the strongest bases, which are electropositive oxides, and of the strongest acids, which are electronegative oxides. This view leads to the conclusions that

"What we call chemical affinity is nothing but the action of the electric polarities of the particles, and electricity is the first cause of all chemical activity." "Every chemical action," Berzelius said, "is at bottom an electrical phenomenon, founded on the electric polarities of the particles."

The tendency is always towards the most complete neutralization of polarities. Secondary causes, such as relative solubility, greater or less volatility, and the like, are often at work, and many chemical actions are not dependent solely on the degrees of polarization of the reacting substances. If a substance combines with another less electropositive than itself, it can be displaced from the compound only by electropositive substances; the more electronegative of two substances which combine can be displaced from the combination only by electronegative substances. For instance, sulphur is positive in sulphuric acid, and can be removed from that acid only by positive substances; sulphur is negative in lead sulphide, and can be removed from that compound only by substances which are more negative than sulphur relatively to lead.

"If these electrochemical views are correct, it follows that every chemical compound is wholly and solely dependent on two opposing forces, positive and negative electricity, and, as there is no third force at work, every chemical compound must be composed of two parts united by the agency of their electrochemical reaction. Hence, whatever the number of its constituents, every compound substance can be divided into two parts, one of which is positively, and the other negatively, electrical. Sulphate of soda, for instance, is not put together from sulphur, oxygen, and sodium, but from sulphuric acid and soda, each of which can be separated into an electropositive and an electronegative constituent. Similarly, alum is not to be thought of as immediately formed from its simple constituents, but as the product of the reaction between sulphate of alumina, as negative element, and sulphate of potash, as positive element. The electrochemical view justifies what I

have already said regarding compound atoms of the first, second, third, etc., order." [1]

When we realize how essential the hypothesis of compound radicals was to the all-embracing dualistic classification of Berzelius, we can understand his enthusiastic reception of the work of Wöhler and Liebig on the compounds of the ternary radical benzoyl.

If we can imagine the shock Berzelius must have received when he realized, in a soberer moment, what he had done when carried away by his enthusiastic welcome of the day-dawn, we may be able to appreciate the righteous indignation wherewith, a few years later, he banned benzoyl, that "compound ternary atom of the first order," from the companionship of the true radicals; for by accepting benzoyl chloride ($C_{14}H_{10}O_2.Cl_2$) as a compound very similar chemically to oil of bitter almonds ($C_{14}H_{10}O_2.H_2$), and by suggesting the formulæ B_zCl_2 and B_zH_2 to emphasize this close relationship, he had implicitly acknowledged that the very negative element chlorine may be substituted by the positive element hydrogen, and hydrogen by chlorine, without a change of the fundamental chemical character of the two compounds. Nearly twenty years had to pass, twenty years marked by a raging, tearing controversy, before chemists were convinced that the substitution of a positive element by a negative element may happen without a profound change of chemical character. When this fact was realized, the system of electrodualism disappeared.

In the years 1839 to 1843, Bunsen [2] published a series of memoirs wherein free use was made, and successfully made, of the compound radical, as an instrument for co-ordinating the relations between organic compounds. Bunsen prepared and analyzed a great many compounds; he studied their reactions and expressed their relations by regarding them as compounds of the radical $C_4H_{12}As_2$, which he isolated, named *kakodyl*, and represented by the abbreviated symbol Kd. (The word is usually spelt *cacodyl* in English books; it is formed from the

[1] Translated from Berzelius' *Lehrbuch der Chemie*, vol. iii, Part I, p. 79 [1825].
[2] "Untersuchungen über die Kakodylreihe," *Annal. Chem. Pharm.*, **31**, 175 [1839]; **37**, 1 [1841]; **42**, 14 [1842]; **46**, 1 [1843].

Greek $\kappa\breve{\alpha}\kappa\acute{\omega}\delta\eta\varsigma$ = ill-smelling). The following formulæ were given by Bunsen to some of the compounds which he investigated: Kd; KdO, KdS, KdSe, KdTe; $KdCl_2$, $KdBr_2$, KdI_2, KdF_2; $KdO.2HgCl_2$, $KdO.3KdI_2$; $KdO.KdO_3$, $3KdO.AgO$, $KdO.xSO_3$; $KdS.KdS_3$; $KdS_3.Au_2S$, $3KdS_3$. Sb_2S_3.

In their memoir on benzoyl compounds (in 1832), Wöhler and Liebig said that "the place of the hydrogen in oil of bitter almonds, or of the oxygen in benzoic acid, can be taken by chlorine, bromine, iodine, sulphur, and cyanogen." They established some chemical likeness between the compounds produced by these reactions, by showing that they are all decomposed by water with the formation of benzoic acid and a hydrogen acid. This was the beginning of the hypothesis of chemical types, an hypothesis destined to grow into a theory which destroyed the system of electrodualism. Let us trace the main lines of its development. The men to be most honoured here are Dumas, Laurent, and Gerhardt.

In 1834,[1] Dumas studied the reactions between chlorine and alcohol, and prepared chloral which he showed to be chlorinated aldehyde, similar to aldehyde in many of its reactions. Some time before 1838, the same chemist prepared chloracetic acid by the interaction of chlorine and acetic acid;[2] in 1838 he confirmed his earlier results and determined the composition of the acid to be $C_8H_2Cl_6O_4$, acetic acid being $C_8H_8O_4$ (C = 6, O = 16). These formulæ recognized that the formation of chloracetic acid from acetic acid consisted in the replacement of six equivalents of hydrogen by six equivalents of chlorine. But at that time (1838) Dumas did not admit that the chlorine in chloracetic acid plays the same part as the equivalent quantity of hydrogen in acetic acid. He said: "To represent me as saying that the hydrogen removed (from acetic acid) is replaced by chlorine, which *plays the same part as* the hydrogen, is to attribute to me an opinion against which I protest vehemently."[3] A year later, Dumas[4] described chloracetic acid and many of its salts

---

[1] *Annal. Chim. Phys.*, (2), **56**, 113 [1834].

[2] In a note in *Compt. rendus*, **7**, 474 [1838], Dumas says he had obtained chloracetic acid some time before; but he now (1838) had prepared it pure.

[3] *Compt. rendus*, **6**, 699 [1838].

[4] "Sur le constitution de quelques corps organiques et sur la théorie des substitutions," *Compt. rendus*, **8**, 609 [1839].

in detail, examined its reactions, and established a very close similarity between this acid and acetic acid from which it is derived. In this memoir Dumas stated the empirical law of substitution and the principle of the maintenance of chemical type. The next year (1840) he developed his ideas concerning chemical types.[1]

"When one treats an hydrogenized organic substance by chlorine, bromine, iodine, or oxygen, etc. these bodies generally remove hydrogen from the substance, and one equivalent of chlorine, of bromine, of iodine, or of oxygen is fixed in the compound for each equivalent of hydrogen that is removed."

Dumas insisted that this statement, which he called *the law of substitution*, is merely an expression of facts established by experiments. He said that the law holds good only in reactions whereby compounds are produced that belong to the same chemical type as those from which they are derived. In the formation of products which are not chemically like the parent compounds, sometimes hydrogen is lost, Dumas said, and nothing is gained, sometimes the quantity of chlorine (or other element) gained is more than equivalent to that of the hydrogen which is lost.

Dumas extended the law of substitution to the replacement of hydrogen, equivalent by equivalent, by various compound radicals, for example, Cy, CO, SO_2, NO_2, and NH_2.

What did Dumas mean by "maintenance of the chemical type"?

"I consider as belonging to the same chemical type those substances which contain the same number of equivalents united in the same manner and have the same fundamental chemical properties."

When the chemical type is maintained, he says that "the molecule remains intact, forming a system wherein one element has simply taken the place of another." Again, he says that the theory of types "considers organic compounds as formed of particles which may be replaced, or displaced, without, so to speak, destroying the original substance."

[1] "Mémoire sur la loi des substitutions et la théorie des types," *Compt. rendus*, **10**, 149 [1840]. "Sur les types chimiques," (1) *Annal. Chim. Phys.*, (2), **73**, 73; (2), *ibid.* (2), **73**, 113 (Dumas and Stas); (3), *ibid.* (2), **74**, 5 (Dumas and Péligot) [1840]. The quotations in the text are translations from the memoir in *Compt. rendus*.

The law of substitution was a purely empirical expression of facts; the theory of types was an attempt to co-ordinate many facts by the help of an image borrowed from the marking of different articles with a common sign.

"The substitution of an element for another, equivalent by equivalent," Dumas said, "is the effect; the preservation of the type is the cause."

Substances belong to the same type when they "contain the same number of equivalents united in the same manner." But how can one discover whether the equivalents are united in the same or in a different manner? Dumas replied: "Substances of the same chemical type are those which show the same fundamental reactions." [1] He spoke of "that community of reactions which one may regard as the best indicator of similar molecular predisposition."

The "same fundamental reactions" are shown, according to Dumas, only by compounds which are formed of the same number of equivalents, and the identity of reactions proves that the equivalents are "united in the same manner" in the different compounds. As examples of "fundamental chemical properties," Dumas described the interactions of alkalis with acetic and with chloracetic acid: acetic acid forms carbonic acid and marsh gas (C_4H_8 in Dumas' notation); chloracetic acid produces carbonic acid and chloroform ($C_4H_2Cl_6$). If the relations between marsh gas and chloroform are expressed by saying that these compounds belong to the same chemical type, the formulæ being C_4H_8 and $C_4H_2Cl_6$, then the compositions of the compounds which can be formed by the interaction of marsh gas and chlorine are known, and are expressed by the following formulæ;

$$C_4H_8 \qquad C_4H_6 \qquad C_4H_4 \qquad C_4H_2 \quad \text{and} \qquad C_4Cl_8.$$
$$Cl_2 \qquad Cl_4 \qquad Cl_6$$
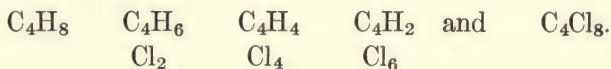
Hydrogen and chlorine play the same part, in chloroform and marsh gas, in acetic and chloracetic acid.

Having demonstrated the similarities between the reactions of acetic acid and those of chloracetic acid, Dumas expressed

[1] This quotation, and those which follow, are from the memoir on chemical types in *Annal. Chim. Phys.* (see foot-note, p. 251).

the compositions of the two acids by similar (dualistic) formulæ, namely;

$$Acetic\ acid \qquad C_4O_4.\ C_4H_2H_6$$
$$Chloracetic\ acid \quad C_4O_4.\ C_4H_2Cl_6.$$
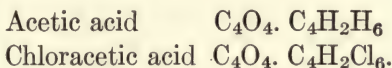
He then gave the following table.

BaO	BaCl$_2$	BaS	BaCy$_2$, etc.
SrO	SrCl$_2$	SrS	SrCy$_2$, etc.
PbO	PbCl$_2$	PbS	PbCy$_2$, etc.
CaO	CaCl$_2$	CaS	CaCy$_2$, etc
MgO	MgCl$_2$	MgS	MgCy$_2$, etc.

The compounds in a vertical series are marked by identity of the non-metallic element, and those in a horizontal series by identity of the metallic element: there are many characteristics common to the compounds of each vertical series, and many common to those of each horizontal series.

Dumas then arranges several organic compounds in a manner similar to that of the foregoing table. Here are some examples of his classification.

C_8H_6 H_6	C_8H_6 Cl_6	C_8H_6 O_3	Etc.
C_4H_2 H_6	C_4H_2 Cl_6	C_4H_2 O_3	C_4O O_3, etc.
$C_{28}H_{10}$ H_6	$C_{28}H_{10}$ Cl_2 O_2	$C_{28}H_{10}$ O_3	Etc.
$C_{24}H_6$ H_6	$C_{24}H_6$ Cl_6	$C_{24}H_6$ O_3	$C_{24}H_4O$ O_3, etc.

Dumas compared the organic radicals C_8H_6, C_4H_2, $C_{28}H_{10}$, etc., with the metals of inorganic compounds. He said that his typical arrangement suggested experimental investigations, and would lead to "a natural classification of organic compounds." He also examined the reactions which establish relationships between alcohols, aldehydes, ethers, and acids, and summarized his results in formulæ which represented the compounds arranged under certain types.

Of the work done by others than Dumas on the subjects of

substitution and chemical types in the thirties and forties of last century, the most important was that of Laurent. That very original man, who seems to have possessed those sharp-cornered eccentricities of temper which are often supposed to accompany genius, published many memoirs on the interactions of chlorine and hydrocarbons, more particularly naphthalene, and on reactions allied to these, from the year 1833 until his death in 1853. I give references to some of the earlier memoirs in a foot-note.[1] In the preface to his book, *Méthode de Chimie* (published in 1854, after his death), Laurent says that "the successive developments I have given to my system have finished by throwing my memoirs into such confusion that several of my friends exacted from me a promise to put a stop to this state of things." To fulfil that promise he "united and coördinated the materials of his work" in a book [2] which bears the stamp of genius.

Laurent admitted Dumas' law of substitution, and gave Dumas the credit of stating that empirical expression of facts; all that was original and suggestive, all that opened lines of investigation in the theory of chemical types, Laurent claimed as his own.[3] Dumas allowed that Laurent had insisted on the identity of the parts played by chlorine and hydrogen in various compounds at a time when he himself strongly opposed that view; but he asserted that Laurent's speculations were premature, because the results of experiments had not pronounced positively in their favour.[4]

Laurent insisted that the law of substitution was too limited. To Dumas' statement

"Whenever chlorine, bromine, nitric acid, or oxygen exerts a dehydrogenizing action on a compound of carbon and hydrogen, each equivalent of hydrogen that is removed is replaced by one equivalent of chlorine, of bromine, or of oxygen"

---

[1] *Annal. Chim. Phys.*, (2), **52**, 275 [1833]; **59**, 196 [1835]; **61**, 125 [1836] **63**, 27, 207, 377 [1836]. *Compt. rendus*, **10**, 409 [1840]. The later memoirs of Laurent are in *Compt. rendus*, and some in *Annal. Chim. Phys.*

[2] All references to Laurent's book, and all quotations from it, are concerned with the translation into English (made by Odling) which appeared in 1855, with the title *Chemical Method.*

[3] See *Compt. rendus*, cited in the last note but one; also foot-note to pp. 198–200 of *Chemical Method.*

[4] *Compt. rendus*, **10**, 165 [1840].

Laurent added this:[1]

"At the same time, there is formed hydrochloric acid, hydrobromic acid, nitrous acid, or water, which is sometimes disengaged, and sometimes remains united with the new radical that is formed."

From this starting-point, Laurent developed his hypothesis of *fundamental and derived radicals.* He insisted that a series of compounds might belong to the same chemical type, might show close similarities of chemical functions, although they did not contain the same radical. He imagined a *fundamental radical* from which various chemically similar compounds were derived; and he represented these compounds as containing different *derived radicals* which were formed by replacing hydrogen in the fundamental radical by equivalent quantities of chlorine, bromine, oxygen, etc., etc. The derived radicals played the same part as the fundamental radical; therefore the relations between the various compounds were suitably suggested by saying that the same chemical type was maintained in all of them.

In his work on derivatives of naphthalene, Laurent had shown that the quantity of chlorine, oxygen, etc., substituted for hydrogen was sometimes more than was equivalent to the hydrogen removed. And here, he said, was seen the importance of his addition to Dumas' law of substitution (quoted above). The excess of chlorine, etc., combined with the derived radical which was formed by substitution, and the new substance was a compound of that derived radical with chlorine, oxygen, or some other element or group of elements. This conception of the processes in question led Laurent to distinguish between elements and groups of elements in the radical and those outside the radical. He noticed differences between the chemical functions of different portions of the chlorine, etc., in naphthalene derivatives.

"If chlorine is placed outside the radical, one can remove it by potash; if it is in the radical, it cannot be removed by potash." "When oxygen is placed outside the radical, the combination becomes acid."[2]

Laurent's hypothesis of fundamental and derived radicals

[1] *Annal. Chim. Phys.*, **60**, 220 [1835].
[2] *Ibid.*, (2), **63**, pp. 42 and 208 [1836].

included Dumas' law of substitution and the hypothesis of chemical types. It went further than these. Although somewhat fanciful, it was an engine which took a large share in the work of battering down the walls of the citadel of electrodualism. Moreover, the conception of substitution inside and outside a radical, and the attribution of different chemical functions to the same element, according to its position within or without the radical, have borne much fruit in modern times. In his exposition of the dualistic scheme of classification, Berzelius recognized the possibility of substituting an element or a radical in a compound by another element or by another radical; but he limited the range of these processes of substitution. Let there be a compound, AB, where A and B are elements or compound radicals; if A is electropositive relatively to B, the Berzelian scheme asserted that A can be substituted only by elements or radicals which are more positive than B, and it declared that only those elements or radicals which are negative relatively to A can be substituted for B. Here is an example. In sulphuric acid (that is, the compound now called sulphuric anhydride, SO_3), sulphur is positive towards oxygen; in lead sulphide, sulphur is negative relatively to lead: the sulphur in sulphuric acid can be substituted only by substances which are more positive than oxygen, and substances which are able to take the place of sulphur in lead sulphide must be more negative than lead.

According to the Berzelian doctrine, every compound is formed by the union of two radicals, simple or compound, which exhibit opposite electrical polarities, and the formation of a compound is always accompanied by the neutralization, more or less complete, of these polarities. If a markedly electronegative radical could take the place of a positive radical in one of the two constituent parts of a compound, both the nature and the intensity of the polarity of that constituent would be changed; therefore the two parts would cease to neutralize each other and could no longer remain united; in other words, the product of this process of substitution could not possibly belong to the same chemical type as the parent compound, from which it must differ both in composition and in reactions.

In his memoir on chemical types, in 1840, Dumas very severely criticised the doctrine of electrodualism.[1] He began by stating the fundamental difference between the system of electrodualism and the system of types. The question to be answered is this: "Does a chemical compound form a simple edifice or a double building?"

"The *nature* of their elementary particles must determine the fundamental properties of bodies, according to electrochemical views; but, in the theory of substitution, it is from the *situation* of these particles that the properties are more particularly derived."

Concerning the necessity, postulated by electrodualism, of regarding every compound as constituted of a positive and a negative, simple or compound particle, Dumas said:

"Never was there an opinion more fitted to impede the progress of organic chemistry. All the difficulties we have experienced for many years in investigating the fundamental formulæ of bodies, the discussions, the misunderstandings, the errors, spring from the prepossessions which that view produced in our minds."

Dumas then gave instances of the strange expedients to which the electrodualists resorted in order to make compounds appear to be formed of two electrically opposed parts, and of their disregard of reactions which established the similarities or the differences between compounds.

Dumas insisted that the theory of substitution and types does not declare the electric properties of substances to be without influence on their chemical properties.

"Only, one is forced to acknowledge that the rôle of electricity can be observed at the moment when the combinations are formed. at the moment when they break up. But, when the elementary molecules have attained equilibrium, we no longer know how to define the influence their electric properties are able to exert, and no one has yet expressed views on this subject which are in accord with experience."

Dumas concluded his memoir thus:

"I would say that in chemistry the nature of the molecules their weights, their forms, and their positions, must exert, each for itself, a real influence on the properties of bodies. It is the influence of the nature of the molecules that has been so well described by Lavoisier; it is that of their weights which Mr. Berzelius has characterized by his immortal labours. One may say that the discoveries of Mr. Mitscherlich refer to the forms of the molecules; and the future will prove whether the work now being conducted by the

---

[1] *Compt rendus*, **10**. 149 [1840].

French chemists is destined to give us the key to the part which belongs to their position."

It is important to notice that many of the chemists who were studying processes of substitution, classification by types, and the uses of compound radicals, in the second quarter of the nineteenth century, preferred to speak of the substitution of elements and radicals by equivalents of other elements and radicals, and of the number of equivalents of each element in this or that compound radical, rather than to express their results and their hypotheses in terms of atoms and molecules. But, while this is true, it is also true that the instruments these chemists were using were instruments of research constructed by the atomic and molecular theory. While they spoke of equivalents, they thought, probably often unconsciously, of small particles. The quantity of an element expressed by its symbol was called an equivalent, and was thought of as the weight of a minute particle; when a formula was given to a compound, that formula called up a mental picture, often dim and blurred in its outlines, of a little mass of the compound.

In Chapter IV we saw that failure followed on every attempt to find a purely chemical method of determining what multiples of the smallest values of the combining weights of elements are the most suitable values for the reacting units of the elements, and that the most suitable values for the reacting units of compounds could not be determined by purely chemical reasoning on the reactions of compounds. Not until Avogadro's hypothesis was realized, and the distinction between atoms and molecules was brought home to chemists, was the problem solved of expressing the compositions of compounds by consistent formulæ. We shall see immediately that the solution of the problem of suggesting the typical, or fundamental reactions of compounds by the formulæ given to them was hastened by using, and boldly using, the atomic and molecular theory as a guide. The gathering of facts concerning substitution brought into greater prominence the system which sought to exhibit the relations between both the compositions and the reactions of compounds by arranging them under certain types. As new processes of substitution, without change

of type, were brought to light, the difficulty increased of reconciling the facts with the fundamental postulates of the Berzelian doctrine of dualism.

The attempts which were made to reconcile the system that was commended to chemists by the tremendous authority of Berzelius with the facts which were discovered concerning substitution, and concerning the reactions of compounds, led to many strange results. Wöhler and Liebig had warned chemists, in 1832, of the dangers that attend the making of formulæ; Berzelius himself had said that "confusion like that of Babel" must follow the manufacture of formulæ which are not based on "ideas that have some claim to be acknowledged as proved facts." But chemists forgot the necessity of thoroughly examining the reactions of compounds before attempting to classify them. When the relations between a series of compounds had been superficially investigated, one chemist would regard certain relations of primary importance, and express these by manipulating the empirical formulæ of the compounds and inventing compound radicals which gave an appearance of completeness to the results of his rough guesses; another chemist would select the same relations and make them appear altogether different by expressing them in other formulæ which contained compound radicals as fanciful as those of his opponent. In his *Chemical Method*, published in 1855, Laurent says (pp. 22, 23):

"Some years back, the discovery of an essence was announced (salicylic ether), which essence contained $C_9H_{10}O_3$; at the same instant, without waiting for further inquiries, it was at once set down as a hydrated oxide, $3C_3H_2.O.2H_2O$. Subsequently we were told that the substance was an acid, and its formula quickly became $C_{18}H_{18}O_5.H_2O$. Some days after, the essence was found to ·be an ether, and in the twinkling of an eye the following arrangement was given, $C_{14}H_{10}O_5C_4H_{10}O$; or, better still, this, $C_2O_4(C_{12}H_{10}).C_4H_8+H_2O$,[1] from which we learn that C_{12} and H_{10} are in intimate combination, while C_2 and O_4 are united in an ordinary manner that C_2O_4 is copulated with $C_{12}H_{10}$- that $C_2O_4(C_{12}H_{10})$ is conjoined with C_4H_8- and, lastly, that the whole forms a marriage of convenience with H_2O!! Have we at least, I will not say a rule, but even a convention, which can determine in this way the arrangement of atoms? No: every chemist follows his own particular course, and changes his formulæ as often as he obtains a new reaction. We should arrive at results

---

[1] This formula is given on p. 23 of *Chemical Method*, but it is one oxygen atom short.

quite as satisfactory by putting the atomic letters of a formula into an urn, and then taking them out, haphazard, to form the dualistic groups."

The Berzelian dualists asserted that if hydrogen is substituted by chlorine, the chemical character of the product must be entirely different from that of the original compound. In his *Chemical Method*, Laurent brings forward instance after instance of the replacement of hydrogen by chlorine without change of chemical type; he describes the reactions of the parent compounds and of the chlorinated derivatives, and shows the great similarities between these substances. The dualists were furious. As Laurent said:

"Experiments went for nothing; dualism had sworn to uphold its position . . . I was an impostor, the worthy associate of a brigand (Gerhardt), etc., etc., and all this for an atom of chlorine put in the place of an atom of hydrogen, for the simple correction of a chemical formula!"

In one of his memoirs, Gerhardt had spoken of various compounds produced by the reactions between acids and alcohols, hydrocarbons, etc., as *"copulated bodies"*: he said that when these compounds are formed, water also is produced, and that these compounds react with water to re-form the acids and the other compounds by the interactions of which they have been obtained. The dualists seized Gerhardt's expression, emptied it of meaning, filled it with fantasies, and used it constantly.

"From this time everything was copulated. Acetic, formic, butyric, margaric, etc., acids,—alkaloids, ethers, amides, anilides, all became copulated bodies. So that to make acetanilide, for example, they no longer employed acetic acid and aniline, but they re-copulated a copulated oxalic acid with a copulated ammonia. I am inventing nothing—altering nothing. Is it my fault if, while writing history, I appear to be composing a romance? What then is a copula? A copula is an imaginary body, the presence of which disguises all the chemical properties of the compounds with which it is united. Thus margaric acid contains oxalic acid united to the copula $C_{32}H_{66}$; and butyric acid, oxalic acid united to the copula C_6H_{14}. But, it may be asked, what proof is there that margaric and butyric acids contain oxalic acid? It is precisely because there is no proof, that they do contain it. We have just said that copulæ disguise the properties of the bodies to which they are united. If, by any reaction, we could render probable the existence of oxalic acid in margaric acid, this reaction would prove that margaric acid was not a copulated body. Reactions are quite incapable of unravelling the mystery; nought but the penetrating spirit of dualism will suffice." [1]

---

[1] *Chemical Method*, p. 204.

Laurent then compares his formulæ for acetic and chlor-acetic acids, $C_2H_4O_2$ and $C_2Cl_3HO_2$, with the dualistic copulated formulæ, $C_2H_6(C_2O_3).H_2O$ and $(C_2Cl_6)C_2O_3.H_2O$; shows that the dualists really admitted a similarity of arrangement of the atoms in the two acids, and that, therefore, they ought to admit a similarity of reactions. "Only, to disguise your defeat," he exclaims, "you clothe your formulæ with copulæ, and affect to understand the real arrangement of the atoms. . . . Come what may, however, the substitution of chlorine for hydrogen is henceforth an admitted fact." [1] He might have added, the substitution of chlorine for hydrogen without change of chemical type was admitted twenty years ago by the founder of electro-dualism.

Williamson's memoir on etherification,[2] published in 1852, did much to advance the use of chemical types, and therefore to undermine the dualistic system. Williamson showed that the relations between alcohols and ethers are expressed, simply and consistently, by the formulæ $\left.\begin{array}{c}H\\R\end{array}\right\}O$ and $\left.\begin{array}{c}R\\R'\end{array}\right\}O$, where R and R' are radicals which may be the same or different. He expressed the relations between sulphuric acid and metallic and ethereal sulphates by the formulæ $\left.\begin{array}{c}H\\H\end{array}\right\}SO_4$, $\left.\begin{array}{c}H\\M\end{array}\right\}SO_4$, and $\left.\begin{array}{c}H\\R\end{array}\right\}SO_4$; and he referred all these compounds to the water-type $\left.\begin{array}{c}H\\H\end{array}\right\}O$. Williamson said:

"The method here employed of stating the rational constitution of bodies by comparison with water, seems to me to be susceptible of great extension; and I have no hesitation in saying that its introduction will be of service in simplifying our ideas, by establishing a uniform standard of comparison by which bodies may be judged of."

Williamson referred acetic acid to the water-type, and asserted that the formula $\left.\begin{array}{c}H\\C_2H_3O\end{array}\right\}O$ expressed the reactions and relations of this compound.

Kolbe [3] criticised what he called Williamson's "acid-theory,"

[1] *Chemical Method*, p. 205.
[2] "*Theory of Etherification*," *Quart. Journ. C. S.*, **4**, 106, 229 [1852].
[3] "Critical observations on Williamson's Theory of water, ethers, and acids," *Quart. Journ. C. S.*, **7**, 111 [1855].

and Williamson replied in a most interesting and amusing manner.[1] Kolbe proposed to find a clear presentation of the relations of acetic acid to other compounds in the formula $(C_2H_3)C_2, O_3.HO$. Here are five kinds of combination, Williamson said:

"Not one of these can be shown to have any existence, so that the formula of one of the simplest of organic bodies is confused by the introduction of unexplained symbols for imaginary differences in the mode of combination of its elements." Kolbe would describe an oak-tree as made up of "chips and blocks and shavings to which it may be reduced by the hatchet." "A Kolbe botanist," Williamson said, "would say that half the chips are united with some of the blocks by the force *parenthesis*; the other half joined to this group in a different way, described by a *buckle*; shavings stuck on to these in a third manner, *comma*; and finally, a compound of shavings and blocks united together by a fourth force, *juxtaposition*, is joined to the main body by a fifth force, *full stop*."

The prophecy made by Berzelius, and forgotten by the man who made it, had come true: Babel and babble had come again. Electrodualism, like so many other attempts to draw boundary lines in nature, had proved itself to be too definite and too vague: too definite, in its classification of all compounds as binary structures; too vague, because it allowed and encouraged a crowd of inexact hypotheses, loosely and hurriedly formed for the purpose of maintaining an appearance of symmetry. Nevertheless, electrodualism, like the hypothesis of phlogiston, was simple and comprehensive; it was "something to fall back on"; it was sealed with the sign-manual of Berzelius; it saved chemists the trouble of thinking for themselves. Electrodualism was a most comforting doctrine. Chemists were unwilling to let it go; for, if it went, what remained?

When the same investigator to-day expressed the relations of a compound by a formula which yesterday he had declared to be impossible, and to-morrow he abandoned, chemists became tired of the pastime of formula-forming. Surely, they said, the same compound cannot have a dozen formulæ; what is the meaning of formulæ?

In the fourth volume of his *Traité de chimie organique*, published in 1856, Gerhardt insisted that formulæ could not do more,

at that time, than express the reactions and the relations of compounds;[1] he said the time had not come for attempting to represent the arrangements of atoms and of molecules by formulæ. "Rational formulæ," Gerhardt said, "are a kind of contracted equations." A compound may have several rational formulæ; that formula is the best which expresses the greatest number of important reactions, and expresses them clearly and intelligibly with the help of a few simple conventions which can be used always. Gerhardt proposed to represent by the formula of a compound the composition of that mass of it which occupies in the gaseous state twice the volume occupied by unit weight of hydrogen. Laurent followed Gerhardt in the use of two-volume formulæ. In *Chemical Method* (p. 72) he says:

"By following out the system of volumes, we obtain *the formulæ which afford the greatest degree of simplicity; which best recall the analogies of the bodies; which accord best with the boiling point and isomorphism; which allow the metamorphoses to be explained in the most simple manner, etc., and in a word, satisfy completely the requirements of chemists.*"

Laurent compared some of the dualistic formulæ with the two-volume formulæ of the same compounds which Gerhardt and he proposed to use. The following are some of the examples cited by Laurent.[2]

	Dualistic Formulæ.		Two-volume Formulæ.
Aldehyde.	$C_4H_6+O+H_2O$	$= 4$ vols.	$C_2H_4O \quad =2$ vols.
Chloraldehyde. . . .	$(C_4H_6.Cl_6)+2(C_4H_6.O_3)$	$=12$ "	$C_2H_3ClO =2$ "
Bichloraldehyde .	$(C_2Cl_6)+(C_4H_6.O_3)$	$= 6$ "	$C_2H_2Cl_2O=2$ "
Trichloraldehyde.	$(C_4H_6)2CO_3+3(C_2Cl_6)$	$=12$ "	$C_2HCl_3O =2$ "
Perchloraldehyde	$CO+CCl_4$	$= 2$ "	$C_2Cl_4O \quad =2$ "
Acetic acid.	$C_4H_6(C_2O_3).H_2O$	$= 4$ "	$C_2H_4O_2 \quad =2$ "
Chloracetic acid. .	$(C_2Cl_6)C_2O_3.H_2O$	$= 4$ "	$C_2HCl_3O_2=2$ "

As Laurent said, these dualistic formulæ "represent a series of hypotheses and nothing else whatever"; the two-volume formulæ cause the facts to stand forth visibly, the facts being "that all these bodies belong to the same series, passing and repassing from one to the other, and that in a certain sense they are but varieties of one and the same substance, as the thousand

---

[1] *Traité de chimie organique*, tome iv, pp. 561 onward [Paris, 1856].
[2] *Chemical Method*, pp. 71, 72.

forms of carbonate of lime are but varieties of the rhombohedron."

The adoption of two-volume formulæ did much to advance the unitary hypothesis, which regarded every compound to be "a simple edifice, not a double building." [1]   The unitary hypothesis tried to express the relations of similar compounds by the machinery of types.   But it was not until chemists had accustomed themselves to think of the reactions of compounds as the reactions of molecules, and the reactions of molecules as conditioned by the arrangements of their parts, the arrangements of atoms and groups of atoms, that the unitary hypothesis became a fine and powerful instrument for advancing accurate chemical knowledge.   When this change in chemical modes of thought was accomplished, the expression *unitary hypothesis* ceased to be used, because the opposed hypothesis of electro-dualism had disappeared.

The main lines of advance from the atomic theory of Dalton to the molecular and atomic theory of Avogadro have been traced in Chapter IV.   The methods of representing the reactions of compounds as conditioned by the arrangements of the atoms and of the atomic groups which form the molecules of these compounds, rest on the notion of chemical equivalency. The history of that subject will be considered in Chapter X.   I shall conclude this chapter by a survey of some of the memoirs which most powerfully advanced the hypothesis that compounds are "simple edifices," and taught chemists to connect the properties of these simple edifices with their structure.

A memoir "On the Constitution of acids and salts " was published by Odling in 1855.[2]

"The object of this communication," Odling said, "is to show, how all salts, whether acid, neutral, or basic, whether containing metallic protoxides, binoxides, sesquioxides, or teroxides, whether monobasic, bibasic, or tribasic, may be respectively reduced to the type of one or more atoms of water, representing water as $\left. \begin{matrix} H \\ H \end{matrix} \right\} O$."

Odling was content to represent his work as a development of that of Williamson and of Gerhardt.   He based his formulæ

---

[1] Dumas, *Compt. rendus*, **10**, 149 [1840].   [2] *Quart. Journ. C. S.*, **7**, 1.

on "the replaceable, or representative, or substitution values" of atoms of metals, and he recognized that the same atom had not always the same value. Odling expressed "the replaceable value" of an atom by one or more dashes attached to the symbol. The following are examples of the formulæ whereby Odling expressed the reactions and relations of various acids and salts.

Type	$\left. \begin{matrix} H' \\ H' \end{matrix} \right\}$	O''		Type	$\left. \begin{matrix} H'H' \\ H'H' \end{matrix} \right\}$	$2O''$
Anhydrous nitric acid	$\left. \begin{matrix} NO'_2 \\ NO'_2 \end{matrix} \right\}$	O''	Anhydrous sulphuric acid	$\left. \begin{matrix} SO''_2 \\ SO''_2 \end{matrix} \right\}$	$2O''$
Potash	$\left. \begin{matrix} K' \\ K' \end{matrix} \right\}$	O''	Stannic oxide	$\left. \begin{matrix} Sn'' \\ Sn'' \end{matrix} \right\}$	$2O''$
Nitrate of potash	$\left. \begin{matrix} NO'_2 \\ K' \end{matrix} \right\}$	O''	Sulphate of potash	$\left. \begin{matrix} SO''_2 \\ 2K' \end{matrix} \right\}$	$2O''$
Nitrate of lead	$\left. \begin{matrix} NO'_2 \\ Pb' \end{matrix} \right\}$	O''	Trinitrate of lead	$\left. \begin{matrix} Pb'NO'_2 \\ Pb'Pb' \end{matrix} \right\}$	$2O'' =$
					$\left. \begin{matrix} NO'_2 \\ 3Pb' \end{matrix} \right\}$	$2O''$

By replacing hydrogen in one, two, three, and four atoms of water by metals and acidic radicals, Odling obtained formulæ for a great many salts. He said:

"I do not consider it at all necessary to the integrity of these views, that the subordinate compounds indicated in the formulæ should in all cases be considered to have an actual, much more an independent existence. I make use of them only as representing, among the many possible arrangements of the elements, the ones which I consider illustrate the most probable action of the affinities concurring in the production of the salt."

We shall see in the next chapter that, in 1852, Frankland stated and illustrated the general principle of atomic substitution and atomic equivalency, of which Odling's memoir contained some special applications.

The idea contained in Williamson's memoir of 1852, and developed by Odling in 1855, was made a finer instrument of research by Kekulé in 1857.[1] Kekulé divided the elements into classes in accordance with the replacing values of their atoms. Hydrogen, chlorine, bromine, potassium, and some other ele-

---

[1] "Ueber die s. g. gepaarten Verbindungen und die Theorie der mehratomigen Radicale," *Annal. Chem. Pharm.*, **104**, 129 [1857]. Kekulé used the atomic weights: H = 1, O = 16, C = 12, N = 14, etc.

ments he called monobasic or monatomic; oxygen and sulphur were dibasic or diatomic; tribasic or triatomic elements were nitrogen, phosphorus, and arsenic; carbon was classed as a tetrabasic or tetratomic element. Kekulé used three main types of compounds: compounds composed of (1) two monatomic atoms, such as H H and Cl H; (2) one diatomic and two monatomic atoms, such as OH_2 and SH_2; (3) one triatomic and three monatomic atoms, such as NH_3 and PH_3. By combining several molecules, he obtained *multiple* or *mixed* types; for

$$\text{instance,} \quad \begin{matrix} \text{ClH} \\ \text{ClH} \end{matrix} \qquad \left\{ \begin{matrix} \text{H} \\ \text{H} \end{matrix} \text{O} \\ \begin{matrix} \text{H} \\ \text{H} \end{matrix} \text{O} \right. \qquad \left. \begin{matrix} \text{ClH} \\ \text{O}\, \begin{matrix} \text{H} \\ \text{H} \end{matrix} \end{matrix} \right\}$$
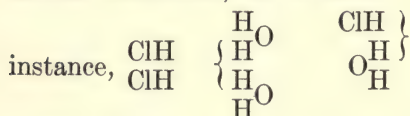
To obtain a compound belonging to a multiple type, it is necessary, Kekulé said, for a polyatomic radical to take the place of two, three, etc., atoms of hydrogen, and thus hold together the molecular structure. For instance, he derived sulphuric acid from the double water-type by replacing 2H by SO_2, and formulated it as $SO_2 \begin{smallmatrix} H_{,,} \\ H \end{smallmatrix} \begin{smallmatrix} O \\ O \end{smallmatrix}$. He formulated urea as $\left. \begin{matrix} CO'' \\ H_2 \\ H_2 \end{matrix} \right\} N_2$
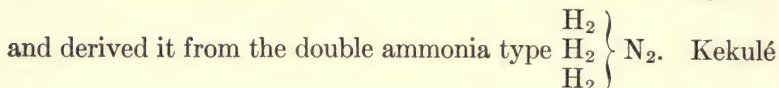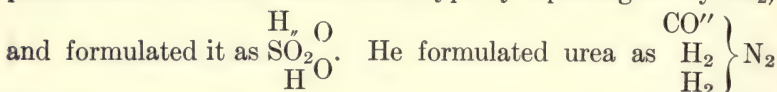
and derived it from the double ammonia type $\left. \begin{matrix} H_2 \\ H_2 \\ H_2 \end{matrix} \right\} N_2$. Kekulé said that two types might be combined by the replacement of hydrogen by a polyatomic radical; for instance, he expressed the relations of hyposulphurous acid (thiosulphuric acid) by the formula $SO_2 \begin{smallmatrix} H \\ H \end{smallmatrix} \begin{smallmatrix} O \\ S \end{smallmatrix}$, and derived it from the type $\left\{ \begin{matrix} H \\ H \end{matrix} O \\ \begin{matrix} H \\ H \end{matrix} S \right.$.
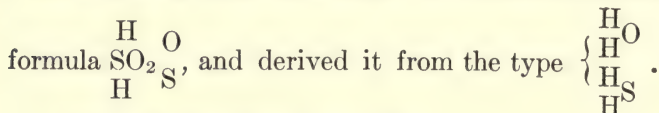
Regarding radicals, Kekulé said:

"In our view, radicals are nothing more than the residues (*Reste*) which remain quite unattacked in a definite transformation. A smaller or a larger radical may be thought of as present in one and the same substance, according as a greater or a smaller part of the group of atoms is attacked."

Taking the case of sulphuric acid, he said that the salts of this acid are formed by replacing two atoms of hydrogen by metals, the acid, therefore, may be described as water the oxygen whereof is replaced by the radical SO_4, and is comparable with

sulphuretted hydrogen: H_2O H_2S H_2SO_4. By the interaction of sulphuric acid and phosphoric chloride (PCl_5) two atoms of oxygen in SO_4 are replaced by chlorine; hence, the radical SO_2 must be thought of as in H_2SO_4. "A decomposition which goes deeper," Kekulé said, "shows that the group which remains unchanged in other reactions (appears as a radical in other reactions) is only the compound of another radical." We see that Kekulé developed formulæ for expressing the reactions and relations of compounds on the bases of types and the atomicity (or basicity) of radicals.[1]

In his book published in 1865,[2] Hofmann followed the lines laid down by Frankland (whose work will be considered in the next chapter), Williamson, Odling, and Kekulé. After giving examples of various reactions, Hofmann said:

"By these particular examples we are led to the general and most important conception of substitution-compounds; that is to say, of bodies formed (often in extensive series) by the replacement of one or more of the constituent atoms of a compound by atoms of some other body introduced in their stead. And we thus make acquaintance, in germ, with a principle, from which, as from a living seed, the mighty fabric of modern chemistry has mainly sprung."[3] Again, Hofmann speaks of "a most general fact of modern chemistry, namely, the uniform retention by substitutional derivative compounds, of the structural type affected by their primary or parent compound."[4]

The structural types most used by Hofmann were the four compounds, HCl, HHO, HHHN, and HHHHC.[5]

Williamson, Odling, Kekulé, and Hofmann did not argue against the dualistic system of Berzelius. They built up another system of classification by boldly applying the molecular and atomic theory to the notion of chemical types introduced into chemistry by Wöhler and Liebig, Bunsen, Dumas, Laurent, and Gerhardt, and, more especially, by making free use of the principle of atomic equivalency which was deduced from experimental evidence by Frankland in 1852. It was the molecular and atomic theory, and especially the hypothesis of atomic

---

[1] Kekulé's memoir will be considered more fully in Chapter XI.
[2] *Introduction to modern chemistry, experimental and theoretic.*
[3] *Lectures*, xii, p. 219
[4] *Lectures*, p 223
[5] Hofmann's work in the development of the notion of atomic equivalency will be considered more fully in Chapter X.

equivalency, which settled the dispute between the dualists and the monists.

Molecules have been thought of as atomic structures during the last fifty years, and this conception has been extraordinarily fruitful, especially in organic chemistry. The types HCl, HHO, HHHN, HHHHC, etc., are molecular types; new molecules are formed by replacing atoms in the typical molecules by other atoms, and by groups of atoms, which are equivalent to those they replace. It is no longer necessary to isolate a radical, a group of atoms, in order to prove the usefulness of the hypothesis of radicals. When we come to examine the history of isomerism (in Chapter XI) we shall see how helpful this hypothesis has proved itself to be.

The settlement of the discussion between the upholders of dualism and those who maintained that compounds are "simple edifices," brought to an end the dispute concerning the constitutions of acids and of salts which had continued since the time of Lavoisier. The view put forth by Davy, and developed by Liebig, held the field; acids were pronounced to be combinations of simple or compound radicals with replaceable hydrogen, and salts to be derivatives of acids formed by exchanging replaceable hydrogen for metals.

The survey which has been made in this chapter and in Chapter VIII of the progress of the study of classification, during the first half of last century, has shown that systems of classification which are based on composition only, or on reactions only, are limited and artificial, and are useful merely for some special purpose; this survey has shown once more that the object of chemistry is to connect changes of the properties, with changes of the compositions of systems of homogeneous substances.

CHAPTER X.

CHEMICAL EQUIVALENCY.

The expression *equivalent weight* of an element has been used repeatedly in Chapters III and IV, generally as synonymous with the expression *combining weight* of an element. Although the value given to the combining weight of this or that element is identical with the value assigned to the equivalent weight of the same element, or is a whole multiple of that value, nevertheless the connotations of the terms *equivalent* and *combining weight* are very different.

The subject of chemical equivalency bears upon many important principles of the science. I shall endeavour, in this chapter, to trace the chief lines along which the study of that subject has moved.

The exchangeability of certain substances, in performing chemical reactions, has been recognized as long as the transmutations of matter have been examined. When chemists began to ask how much of one substance could be exchanged for a determinate quantity of another, the accurate study of chemical equivalency began. The experimental foundation of this part of chemical science was laid, towards the end of the eighteenth century and in the first years of the nineteenth, by J. B. Richter (1762–1807), in two works, entitled (1) *Anfangsgründe der Stöchyometrie oder Messkunst chymischer Elemente* (published in 1792–93 in three volumes), and (2) *Ueber die neurn Gegenstände der Chemie* (published from 1791 to 1802, in eleven parts).

A book by C. F. Wenzel (published in 1777), entitled *Lehre von der Verwandtschaft der Körper,* had a considerable influence in advancing the study of chemical equivalency· but the work

of Wenzel is not comparable with that of Richter, either in accuracy, range, or results.[1]

The second of Richter's treatises is the more important as regards the subject now under consideration.[2]

Richter determined the weights of various bases which neutralized a constant weight of each of several acids; from his results he drew the following conclusion. Let P be the mass of one acid which neutralizes the masses a, b, c, d, and e, of various bases; and let Q be the mass of another acid which neutralizes the masses α, β, γ, δ, and ε, of the same bases; also let the neutral salts $P+a$ and $Q+\beta$, $P+a$ and $Q+\gamma$, $P+c$ and $Q+\alpha$, etc., decompose one another so that the products are neutral; then the ratio of the masses a, b, c, d, and e is the same as the ratio of the masses α, β, γ, δ, and ε.[3]

Of this statement Richter said that it is a true touchstone of experiments on the proportions wherein acids and bases neutralize each other; for if the proportions which are determined experimentally are not in keeping with those demanded by the proposition, they may be rejected as erroneous.[4]

---

[1] Unfortunately, many of those who have written of the history of chemistry have confused the works of Wenzel and Richter, and attributed to the former much of what was done by the latter. Berzelius began the confusion (*Lehrbuch der Chemie*, vol. iii, p. 17 [1827]); the mistake was continued by Kopp (*Geschichte der Chemie*, vol. ii, pp. 356–59 [1844]), but corrected by him in his later book, *Die Entwickelung der Chemie in der neueren Zeit*, p. 250 [1873]. In 1841 appeared a paper by G. H. Hess, entitled *Ueber J. B. Richter's Arbeiten* (*J. prakt. Chem.*, 24, 420), wherein an account was given of the most important portions of Richter's work, and the attribution to Wenzel of the credit of laying the foundation of chemical equivalency was shown to be unfounded.

[2] The copy of Richter's *Ueber die neurn Gegenstände der Chemie* from which I quote was published at "Breslau, Hirschberg u. Lissa in Südpreussen, bey Johann Friedrich Korn, dem Aeltern, der Buchladen in Breslau ist neben dem Königl. Oberzoll- u. Acis-Amt auf dem grossen Ringe."

[3] Richter's words are these (Part IV of *Neurn Gegenstände*, p. 67): "*Lehrsatz.* Wenn P die Masse eines determinirenden Elementes, wo die Massen seiner determinirten Elemente a, b, c, d, e, u. s. w. sind [by *determinirendes Element* Richter means the neutralizing substance of which a constant weight is taken; by *determinirte Elemente* he means the substances neutralized], Q aber die Masse eines andern determinirenden Elementes ist, wo die Massen seiner determinirten Elemente α, β, γ, δ, ε, u. s. w. sind, doch so, dass jederzeit a und α, b und β, c und γ, d und δ, e und ε, einerley Element bezeichnen, und sich die neutralen Massen $P+a$ und $Q+\beta$, $P+a$ und $Q+\gamma$, $P+c$ und $Q+\alpha$, u. s. w., so durch die doppelte Verwandtschaft zerlegen, dass die daraus enstandenen Producte wiederum neutral sind, so haben die Massen a, b, c, d, e, u. s. w. eben das quantitative Verhältniss unter einander, als die Massen α, β, γ, δ, ε, u. s. w., oder ungekehr."

[4] Richter's words are (Part IV, p. 69): "Dieser Lehrsatz ist ein wahrer Probierstein der angestellten sich auf Neutralitäts-Verhältnisse beziehenden versuche; denn, wenn die empirisch aufgefundenen Verhältnisse nicht von der Beschaffenheit

As an example of Richter's use of the *touchstone,* I give the results of his experiments, and his calculations, on the neutralization of ammonia, soda, and potash by hydrofluoric acid. In his *Stöchyometrie,* he found that 1000 parts of sulphuric acid neutralized 638 parts of ammonia, 1218 of soda, and 1606 of potash: in Part IV of *Neurn Gegenstände* he determined that 1000 parts of hydrofluoric acid neutralized 3807 parts of potash.

To find the weights of ammonia and soda neutralized by 1000 parts of hydrofluoric acid, he made these calculations:

(i) 1606 (potash):1218 (soda) = 3807 (potash):x;

(ii) 1606 (potash): 638 (ammonia) = 3807 (potash):x';

$x = 2887$ = weight of soda neutralized by 1000 parts by weight of hydrofluoric acid;

$x' = 1512$ = weight of ammonia neutralized by 1000 parts by weight of hydrofluoric acid.

Richter said that the weights of the three bases—ammonia, soda, and potash—which neutralize a constant weight of hydrofluoric acid are nearly in arithmetical progression. On this assumption, he corrected the numbers obtained experimentally, by substituting 1507 for 1512 as the weight of ammonia neutralized by 1000 parts of the acid. He then gave the following table (p. 72, Part IV).

WEIGHTS OF THE THREE ALKALIS NEUTRALIZED BY 1000 PARTS OF HYDROFLUORIC ACID.

Ammonia $= a$ $= 1507$ $= 1507$
[* $= a + b = 1507 + 460$ $= 1967$]
Soda $= a + 3b = 1507 + 3 \times 460 = 2887$
Potash $= a + 5b = 1507 + 5 \times 460 = 3807$
[* $= a + 7b = 1507 + 7 \times 460 = 4727$]

The second and fifth members of the series are wanting, because, Richter said, "Man zählt bisjetzt nur drey alkalische Salze."

Richter then applied his hypothesis, that the weights of bases neutralized by a constant weight of each of several acids

sind, wie sie das Gesetz der wirklich vorhandenen mit unveränderter Neutralitt begleiteten Zerlegung durch die doppelte Verwandtschaft erfordert, so sind sie ohne weitere Untersuchung als unrichtig zu verwerfen, und es ist alsdenn in den angestellten Versuchen ein Irrthum vorgefallen."

are in arithmetical progression, to correct the numbers he had determined experimentally as being the weights of alumina, baryta, lime, and magnesia severally neutralized by 1000 parts of each of the acids hydrofluoric, hydrochloric, sulphuric, and nitric. He gave a table of which the following is a portion (Part IV, p. 97).

WEIGHTS OF FOUR ACIDS WHICH NEUTRALIZE 1000 PARTS OF MAGNESIA, LIME, AND BARYTA.

		Magnesia.	Lime.	Baryta.
Hydrofluoric acid $=c$	$=$	$696 \cdot 4$	$538 \cdot 5$	$192 \cdot 5$
[*	$=cd$ $=$	$825 \cdot 5$	$638 \cdot 3$	$228 \cdot 2$]
Hydrochloric acid $=cd^3$	$=$	$1160 \cdot 0$	$897 \cdot 2$	$320 \cdot 6$
Sulphuric acid $=cd^5$	$=$	$1630 \cdot 0$	$1260 \cdot 7$	$450 \cdot 1$
Nitric acid $=cd^7$	$=$	$2290 \cdot 4$	$1771 \cdot 5$	$633 \cdot 1$
[*	$=cd^9$ $=$	$3218 \cdot 4$	$2489 \cdot 2$	$889 \cdot 6$]

The second, sixth, and perhaps other members of the series are wanting.

Richter concluded that the weights of acids which neutralize a constant weight of any base are in geometrical progression.

Richter's analyses were certainly not very accurate,[1] and his hypotheses, that the weights of bases neutralized by a constant weight of acid are in arithmetical progression, and the weights of acids neutralized by a constant weight of base are in geometrical progression, were erroneous; nevertheless, the foundation of all that has been done in developing the subject of chemical equivalency was laid by him in the statement, that the proportion between the weights of bases which are neutralized by acids is constant and independent of the nature of the acid, and the proportion between the weights of acids which are neutralized by bases is constant and independent of the nature of the base.

Richter presented his results on the weights of acids and bases which neutralize one another in tables. As one table gave the weights of several acids which saturated 1000 parts by weight of each of two or three bases, another table gave the weights of several bases which neutralized 1000 parts of each of a few acids, and the other tables contained similar data, it is evident that the whole of Richter's results might have been presented in two tables.

---

[1] Richter says he always lost something in his analyses, and he never cared to make a quantitative experiment with less than 500 *gran* of substance.

But Richter might have stated his results in a single table; for he recognized, and acted on the recognition, that measurements of the quantities of one base which saturate the same weight of each of several acids, and the quantities of various bases which saturate the same determinate weight of any one of these acids, give the data for calculating the weight of each of the bases which will saturate any of the acids.[1]

Had Richter presented his results in a single table, that table would have taken the following form.

ACIDS.		BASES.	
Hydrofluoric	423	Lime	796
Hydrochloric	717	Soda	1221
Sulphuric	1000	Potash	1606
Etc.	Etc.	Etc.	Etc.

The number attached to an acid is the weight of that acid which saturates the weight of a base expressed by the number attached thereto.

In 1802, Fischer treated Richter's results in the way I have indicated, and presented them in a single table, as follows.[2]

I. ACIDS.		II. BASES.	
Hydrofluoric acid. ...	427	Alumina	525
Carbonic acid.	577	Magnesia	615
Sebacic acid.	706	Ammonia	672
Hydrochloric acid	712	Lime	793
Oxalic acid.	755	Soda.	859

[1] For instance, Richter said that

2239 parts by weight of potash saturate 1000 parts of hydrochloric acid,
3797 parts by weight of potash saturate 1000 parts of hydrofluoric acid
1606 parts by weight of potash saturate 1000 parts of sulphuric acid;

and that

1882 parts by weight of lime ⎫
1512 parts by weight of ammonia ⎬ saturate 1000 parts of hydrofluoric acid.
2887 parts by weight of soda ⎭

Hence;

$3797(\text{potash}) : 2887(\text{soda}) = 1606(\text{potash}) : x;$

and,

$3797(\text{potash}) : 1882(\text{lime}) = 1606(\text{potash}) : x';$

where $x =$ weight of soda which saturates 1000 parts of sulphuric acid, and
$x' =$ weight of lime which saturates 1000 parts of sulphuric acid.

[2] Taken from a note by Fischer in Berthollet's *Essai de Statique Chimique* (vol. i. p. 134). Fischer used Richter's latest results, some of which differed considerably from his earlier numbers.

I. ACIDS.		II. BASES.	
Phosphoric acid	979	Strontia	1329
Formic acid	988	Potash	1605
Sulphuric acid	1000	Baryta	2222
Succinic acid	1209		
Nitric acid	1409		
Acetic acid	1480		
Citric acid	1683		
Tartaric acid	1694		

This is the first table of *equivalent weights*. The weights of the acids in one column are equivalent, and the weights of the bases in the other column are equivalent, in that these are the weights (according to Richter) which severally neutralize one and the same weight of any base, and one and the same weight of any acid, to form neutral salts.

In 1803, Richter adopted Fischer's way of presenting the results of the analyses of neutral salts, and gave a table of the equivalent weights of eighteen acids and thirty bases.[1]

The ninth part of Richter's *Neurn Gegenstände* is concerned with determinations of the weights of fifteen metals which dissolve in 1000 parts of each of the acids, sulphuric, hydrochloric and nitric, to form neutral salts. He concluded that the weights of the metals were in arithmetical progression, and he used this hypothesis to correct his experimental results. Richter supposed that the metals were first oxidized, and the metallic earths were then dissolved. He called the process of oxidation *die Lebensluftstoffung der Metalle*; and he said that the weight of *Lebensluftstoff* which combines with those weights of metals that saturate a constant weight of an acid is itself constant. This is equivalent to saying, if we use the language of to-day, that those weights of various bases which saturate a constant weight of an acid contain the same weight of oxygen.

The following tables are taken from Part IX, pp. 126, 127 (1798) of Richter's *Neurn Gegenstände*. (See next page.)

Richter was constantly seeking for regularities in the proportions wherein substances react, and endeavouring to express

---

[1] In the article "Neutralität" in Richter's edition of Bourguet's *Chemical Dictionary*.

No. I.

Signs of the metallic substrata.	Form or general expression of the quantitative arrangement of specific neutralizations of metallic substrata, in reference to the three indicated acids.	Specific neutralization of the metallic substrata for each of the following acids whose mass is 1000, numerically expressed.		
		Sulphuric acid. $a=705$ $b=68$	Hydrochloric acid. $a=985\cdot4$ $b=95$	Nitric acid. $a=498\cdot8$ $b=48\cdot1$
♂	a =	705	985·4	498·8
♂	$a+\ \ b$ =	773	1080·4	546·9
♂	$a+\ 2b$ =	841	1175·4	595·0
ô	$a+\ 3b$ =	909	1270·4	643·1
♀	$a+\ 4b$ =	977	1365·4	691·2
♀	$a+\ 9b$ =	1317	1840·4	931·7
☉	$a+10b$ =	1385	1985·4	979·8
☽☉	$a+13b$ =	1589	2220·4	1124·1
♁	$a+14b$ =	1657	2315·4	1172·2
♃	$a+16b$ =	1793	2505·4	1268·4
♇	$a+22b$ =	2201	3075·4	1557·0
♉	$a+29b$ =	2677	3740·4	1893·7
♄	$a+36b$ =	3153	4405·4	2230·4
☽	$a+38b$ =	3289	4595·4	2326·6
☿	$a+70b$ =	5465	7635·4	3865·8

No. II.

Signs of the metallic earths.	Form or general expression of the quantitative arrangement of the specific neutralizations of metallic earths in reference to the three indicated acids.	Specific neutralization of the metallic earths for each of the following acids whose mass is 1000, numerically expressed.		
		Sulphuric acid. $a=705$ $b=68$ $u=439$	Hydrochloric acid. $a=985\cdot4$ $b=95$ $u=612\cdot7$	Nitric acid. $a=498\cdot8$ $b=48\cdot1$ $u=310\cdot7$
♂	$u+a$ =	1144	1599·1	809·5
♂	$u+a+\ \ b$ =	1212	1694·1	857·6
♂	$u+a+\ 2b$ =	1280	1789·1	905·7
ô	$u+a+\ 3b$ =	1348	1884·1	953·8
♀	$u+a+\ 4b$ =	1416	1979·1	1001·9
♂	$u+a+\ 9b$ =	1756	2454·1	1242·4
☉	$u+a+10b$ =	1824	2549·1	1290·5
☽☉	$u+a+13b$ =	2028	2834·1	1434·8
♁	$u+a+14b$ =	2096	2929·1	1482·9
♃	$u+a+16b$ =	2232	3119·1	1579·1
♇	$u+a+22b$ =	2640	3689·1	1867·7
♉	$u+a+29b$ =	3116	4354·1	2204·4
♄	$u+a+36b$ =	3592	5019·1	2541·1
☽	$u+a+38b$ =	3728	5209·1	2637·3
☿	$u+a+70b$ =	5904	8249·1	4176·5

The signs used by Richter have the following meanings

♂ = manganese	♂ = nickel	♂ = iron	ô = zinc	♀ = copper
♁ = antimony	☉ = gold	☽☉ = platinum	♉ = cobalt	♃ = tin
♇ = uranium	♂ = bismuth	♄ = lead	☽ = silver	☿ = mercury.

his results in a general form wherefrom he could deduce the quantitative course of other reactions.

As examples of Richter's methods of experiment and calculation, I give his determinations of the weights of silver nitrate, and silver chloride, obtained by saturating nitric acid with silver, and by adding common salt to a solution of silver in nitric acid.

I. 395 parts of silver, dissolved in nitric acid, evaporated and dried, gave 619 parts of silver nitrate; hence 1000 parts of silver give 1567 parts of silver nitrate. By dissolving silver in acid, precipitating by alkali, and weighing the product, Richter found that

1000 parts of silver combine with 133·5 parts of *Lebensluftstoff*.

Now the difference between 1567 and 1000 = 567; and 567 − 133·5 = 433·5; that is, 1000 parts of silver combine with 133·5 parts of *Lebensluftstoff*, and 433·5 parts of nitric acid, to form (1000 + 133·5 + 433·5) 1567 parts of silver nitrate.

These results were tested as follows.

Richter had determined that the weights of sulphuric and nitric acids which saturate 1000 parts of soda were 1164·7 and 1636·6 respectively (corrected by the hypothesis that the weights of acids which neutralize bases are in geometrical progression), and that 305·8 parts of sulphuric acid saturate 1000 parts of silver.

Hence 1164·7 : 1636·6 = 305·8 : 429·7;

that is, 1000 parts of silver should be saturated by 429·7 parts of nitric acid.

Hence 1000 parts of silver will combine with 429·7 parts of nitric acid and 133·5 parts of *Lebensluftstoff*, and the weight of silver nitrate formed will be the sum of these weights, which is 1563·2, a quantity which agrees well with 1567, the weight obtained by direct experiment.

II. 442 parts of silver dissolved in nitric acid, and precipitated by common salt, gave 588 parts of silver chloride; hence 1000 parts of silver give 1330 parts of silver chloride.

Now, the (corrected) weights of sulphuric and hydrochloric acids which neutralize 1000 parts of soda had been found to be 1164·7 and 828·9 respectively, and 305·8 parts of sulphuric acid had been found to saturate 1000 parts of silver.

Hence 1164·7 : 828·9 = 305·8 : 217·6;

that is, 1000 parts of silver should be saturated by 217·6 parts of hydrochloric acid.

Hence, and from certain data given under I., 1000 parts of silver will combine with 217·6 parts of hydrochloric acid and 133·5 parts of *Lebensluftstoff*, and the weight of silver chloride formed will be the sum of these weights, which is 1351·1, a quantity which agrees well with 1330, the weight obtained by direct experiment.

Nothing comparable with Richter's generalization concerning the constancy of the ratio between the weights of bases which neutralize different acids is to be found in Wenzel's work.

Berzelius, Dumas, and others have given to Wenzel the credit of proving that, when two neutral salts in solution react to produce two new salts in solution which are also neutral, the neutrality is maintained, because the quantity of either base which saturated its acid in the first pair of salts is exactly the quantity which saturates the other acid wherewith the base is combined when the reaction is completed; but, in reality, it was Richter, and not Wenzel, who made this great advance.

I give two examples of Wenzel's treatment of a reaction between two salts, resulting in the formation of two other salts. Wenzel proposed to determine what weights of crystallized copper sulphate and lead acetate should be used for the preparation of copper acetate.[1]

From his determinations of the weight of copper required to saturate sulphuric acid, and the weight of lead required to saturate acetic acid, and also the loss of weight attending the dehydration, by heat, of crystallized copper sulphate and crystallized lead acetate respectively, he concluded that weights of these two salts should be used in the ratio 480:617. If the salts were mixed in that ratio, Wenzel said that the whole of the lead of the lead acetate would combine with the sulphuric acid of the copper sulphate to form lead sulphate which would be precipitated; but he calculated that the quantity of acetic acid in the lead acetate would not be enough to combine with all the copper, and that some of the copper would remain mixed with the precipitated lead sulphate.

Another example of Wenzel's experiments and reasoning on a reaction between two salts is his treatment of the question,[2] How much cinnabar must be mixed with a determinate weight of silver chloride to effect the complete separation of the hydrochloric acid from the silver?

From the results of his experiments on the combination of silver and hydrochloric acid, silver and sulphur, and mercury and sulphur, Wenzel concluded that half an ounce of silver

[1] *Lehre von der Verwandtschaft der Körper*, p. 319. The edition I have used is entitled "Carl Friedrich's Wenzel's Lehre von der Verwandtschaft der Körper, mit Anmerkungen herausgegeben von David Hieronimus Grindel. Dresden, bey Heinrich Gerlach. 1800."
[2] *Lehre*, p. 316.

chloride contained 180$\frac{9}{16}$ grains of silver, and that half an ounce of silver combined with 35$\frac{1}{2}$ grains of sulphur; hence, he said, 180$\frac{9}{16}$ grains of silver will be saturated by 26$\frac{3}{4}$ grains of sulphur, which is the quantity of sulphur contained in 125$\frac{1}{2}$ grains of cinnabar. If, therefore, a mixture of half an ounce of silver chloride with 125$\frac{1}{2}$ grains of cinnabar were heated, the whole of the silver should be changed into silver sulphide.

But Wenzel's experiments on the weight of mercury required to saturate hydrochloric acid led him to conclude that 125$\frac{1}{2}$ grains of cinnabar did not contain enough mercury to combine with the whole of the hydrochloric acid obtainable from half an ounce of silver chloride; he said that 202$\frac{1}{2}$ grains of cinnabar must be used to effect a complete decomposition.

If half an ounce of silver chloride is mixed with 202$\frac{1}{2}$ grains of cinnabar, and the mixture is heated, Wenzel says that the acid of the chloride will combine with the mercury and rise as an acrid sublimate, but the silver will remain combined with only as much sulphur as is contained in 125$\frac{1}{2}$ grains of cinnabar. Wenzel does not say what becomes of the rest of the sulphur; his statement seems to imply that it remains behind when the sublimation is completed.

These examples of Wenzel's investigation of the changes which occur when two salts react to produce two other salts, show that he did not realize that an adequate description of a chemical occurrence must account for the whole of each substance which takes part in the reaction, and that the proportions between the reacting weights of homogeneous substances are constant.

The earlier part of Wenzel's *Lehre von der Verwandtschaft der Korper* is concerned with the general aspects of chemical affinity; his conclusions will be referred to in the chapter on that subject. The greater part of the work is devoted to determinations of the weights of various elements and compounds (12 metals and 9 bases) which saturate different acids (10 acids and 3 mixtures of acids). Many of Wenzel's determinations were very accurate, considering the methods which were available in his day; but he made little use of the results which he obtained.

After the work of Richter, all that remained to be done to complete the examination of the equivalency of acids and bases was to extend, and make more accurate, the determinations of the weights of members of these two classes of compounds which react to form neutral salts. When attempts were made to apply the notion of equivalency to the elements, and to determine the weights of elements which are chemically equivalent, great difficulties were encountered. Dumas put the matter very clearly in his *Leçons*.[1] Take the case of iron: according to Dumas, 100 parts by weight of oxygen combine with 339 of iron to form the protoxide, and with 226 of iron to form the peroxide; is the equivalent weight of iron 339, or is it 226? The convention in use when Dumas wrote (1836) was to take the equivalent of a metal as that weight of it which combines with 100 parts by weight of oxygen to form a protoxide; in the case of iron this would lead to the conclusion that an equivalent weight of the protoxide is composed of one equivalent of iron and one equivalent of oxygen, and an equivalent weight of the peroxide is composed of two-thirds of an equivalent of iron and one equivalent of oxygen. If the symbol Fe represented an equivalent weight of iron, and O represented an equivalent weight of oxygen, then the formula for the protoxide would be FeO, and the formula for the peroxide would be Fe_2O. Or, Fe might represent an equivalent of iron in one oxide, and fe an equivalent of the same metal in the other oxide; then the formulæ of the oxides would be FeO and feO respectively. It was found impossible to establish a consistent and workable system of notation on the basis of the equivalent weights of elements.

In 1852, Frankland[2] applied the notion of equivalency to the atoms of the elements, and thus opened a field of research which has been exceedingly fruitful. Frankland said:

"When the formulæ of inorganic chemical compounds are considered, even a superficial observer is impressed with the general symmetry of their construction. The compounds of nitrogen, phosphorus, antimony, and

---

[1] *Leçons sur la Philosophie chimique*, delivered in 1836. The 5th Leçon is devoted to *équivalents chimiques*.

[2] *Phil. Trans.*, **142**, 417; the memoir is entitled "On a new series of Organic bodies containing metals."

arsenic, especially, exhibit the tendency of these elements to form compounds containing 3 or 5 atoms of other elements; and it is in these proportions that their affinities are best satisfied: thus in the ternal group we have NO_3, NH_3, NI_3, NS_3, PO_3, PH_3, PCl_3, SbO_3, $SbCl_3$, AsO_3, AsH_3, $AsCl_3$, etc.; and in the five-atom group NO_5, NH_4O, NH_4I, PO_5, PH_4I, etc.[1] Without offering any hypothesis regarding the cause of this systematic grouping of atoms, *it is sufficiently evident, from the examples just given, that such a tendency or law prevails, and that, no matter what the character of the uniting atoms may be, the combining power of the attracting element, if I may be allowed the term, is always satisfied by the same number of these atoms."*

The statement in italics was called by Frankland, at a later time, *the law of atomicity.* In a prefatory note to his memoir on "Organo-metallic compounds," in the collected edition of his *Researches,*[2] Frankland said that until Cannizzaro "had placed the atomic weights of the metallic elements upon their present consistent basis, the satisfactory development of the doctrine (of atomicity) was impossible."

Williamson had done something to prepare the way for Frankland's *law of atomicity,* in his paper "On the constitution of Salts," in *The Chemical Gazette* for 1851 (published in abstract in *C. S. Journal,* **4**, 350 [1852]), by representing many chemical transformations as consisting in the substitution of one atom, or group of atoms, for another atom, or atomic group. In the substitutions of which Williamson gave many examples, the equivalency of various atoms and groups of atoms was assumed.

In 1855, Odling[3] gave examples to show that the atoms of certain elements have, each, more than one "replaceable, or representative, or substitution value." He proposed to mark

"these different substitution values, by one or more dashes to the right or left of the symbol . . . thus, H′, an atom of hydrogen, Sn′, an atom of tin, as existing in stannous salts; . . . Sn″, the same atom of tin, . . . existing in stannic salts. . . . " "From this it is evident," Odling said, "that in making equivalent substitutions for 1, 2, or 3 atoms of hydrogen respectively, the number of atoms introduced may vary very considerably, provided the total exponential value remains the same: thus, 3 atoms of hydro-

---

[1] Frankland used the atomic weights: $O=8$, $S=16$, $N=14$, $P=31$, $As=75$, $Sb=122$, $I=127$, $Cl=35 \cdot 5$.

[2] *Experimental Researches in Pure, Applied, and Physical Chemistry,"* by E. Frankland (London, 1877), p. 154.

[3] In a paper entitled "On the Constitution of Acids and Salts" (*C. S. Journal,* **7**, 1).

gen, H'H'H', may be alike perfectly represented by K'K'K', 1½Sn'', Sn'' + K' . . . Bi''' . . . . "

An important memoir was published by Kekulé in 1857.[1] Kekulé said that his communication was merely a development of the leading ideas of Williamson's memoir (already referred to), ideas which had been extended by Odling. Kekulé classified the elements in accordance with the number of atoms, or atomic groups, wherewith one atom of each element combined. He gave examples of three main groups.

    I. Monobasic or monatomic; for instance, H,Cl,Br,K.
    II. Dibasic or diatomic;   for instance, O,S.
    III. Tribasic or triatomic;   for instance, N,P,As.

"Carbon," Kekulé said, "is tetrabasic or tetratomic; that is, 1 atom of carbon = C = 12 is equivalent to 4 atoms of H." He gave examples of polyatomic atoms, or atomic groups, replacing several monatomic, etc., atoms, and thus binding the residues of two or more molecules into one new molecule.

The *Philosophical Magazine* for 1858 contains a very interesting memoir by A. S. Couper, entitled "On a New Chemical Theory." [2] In that memoir Couper insists on the necessity of studying and comparing the properties of compounds for the purpose of finding the parts played by the individual elements.

"There is one leading feature, one inherent property," Couper said, "common to all the elements. It has been denominated chemical affinity. It is discovered under two aspects: (1) affinity of kind, (2) affinity of degree. Affinity of kind is the special affinities manifested among the elements, the one for the other, etc., as carbon for oxygen, for chlorine, for hydrogen, etc. Affinity of degree is the grades, or also limits of combination, which the elements display. For instance, C_2O_2 and C_2O_4 are the degrees of affinity of carbon for oxygen. C_2O_2 may be called the first degree, and C_2O_4 may be termed the second degree,[3] and, as a higher degree than this is not known for carbon, its ultimate affinity or combining limit. . . . Here, then, is an inherent property common to all elements, by the removal of which the chemical character of an element will be destroyed, and by virtue of which an element finds its place marked out in a complex body."

In his lectures delivered in the later years of the fifties (of

---

[1] "Ueber die s. g. gepaarten Verbindungen und die Theorie der mehratomigen Radicale,' *Annal. Chem. Pharm.*, **104**, 129.

[2] *Phil. Mag.* [4], **16**, 104.

[3] Couper used the atomic weights C = 6 and O = 8. In modern formulæ, his two oxides of carbon become CO and CO_2.

the nineteenth century), Cannizzaro dealt in detail with the subject of the equivalency of atoms.[1]

He compared two series of chlorides

(1) $H_2Cl_2, Hg_2Cl_2, Cu_2Cl_2, K_2Cl_2, Ag_2Cl_2$, etc.;
(2) $HgCl_2, CuCl_2, ZnCl_2, PbCl_2$, etc.;

and pointed out that one atom of metal combined, now with one atom of chlorine and now with two atoms of chlorine. "I express that," said Cannizzaro, "by saying that one atom of metal is equivalent, in the first case, to one atom of hydrogen, but in the second case to two atoms of hydrogen." Cannizzaro then compared various reactions, and showed that, as the quantity of chlorine which combines with one atom of zinc, lead, etc., also combines with two atoms of hydrogen, potassium, silver, etc., so is the quantity of oxygen, or of any other element which combines with one atom of zinc, lead, etc., the same as the quantity which combines with two atoms of hydrogen, potassium, silver, etc.

"That proves," Cannizzaro said, "that the property of the first kind of atoms of being equivalent each to two of the second kind of atoms, is dependent on a cause which is to be found either in the nature of the atoms themselves, or in the conditions attending their combination; . . . any atom of the first kind has double the capacity of saturation of any atom of the second kind."

Cannizzaro classed the atoms of elements as monatomic, diatomic, triatomic, etc., according as they are equivalent to one, two, three, etc., atoms of hydrogen or of chlorine.[2]

He insisted on the difference between the law of equivalency and the law of atoms.[3]

"The latter," he said, "asserts that the quantity of an element contained in different molecules must be a whole multiple of one and the same quantity. This law cannot foresee that, for example, one atom of zinc is equivalent to two atoms of hydrogen, not only in the compounds of zinc with chlorine,

---

[1] *Sunto* (German edition), pp. 29–42. (For full title, etc., of *Sunto*, see note, p. 133.)

[2] Cannizzaro mentioned that Gaudin (*Annal. Chim. Phys.* for 1833, pp. 113) had applied the terms *monatomic* and *diatomic* to elementary molecules containing one and two atoms respectively; but he preferred to use the word *atomicity* to express the saturating capacity of atoms.

[3] For details regarding Cannizzaro's treatment of the *law of atoms*, see pp. 135, 136; 139, 140.

but also in all the other compounds into which zinc can enter. The unchangeability of the proportions between the atomic weights of the different bodies which mutually replace one another, whatever be the nature and number of the other constituents of the compounds, is a law which limits the number of possible compounds, and, more especially, applies to all cases of double exchange."

Cannizzaro showed how the capacity of saturation (or the atomicity) of an atomic group is determined; by studying the compositions of molecules composed of that group and atoms of hydrogen, chlorine, bromine, or iodine. He then applied the law of atoms, and the law of the equivalency of atoms, to many reactions. To emphasize the resemblances between similar reactions, Cannizzaro used the symbols R′, R″, R‴, etc., to denote any monatomic, diatomic, or triatomic atom or group of atoms; and he expressed the compositions of molecules composed of several atoms or groups by the symbols $R_a'R_b'$, $R_a''R_b''$, $R_a'R_b''$, $R_a'R_b''R_c'''$, etc.

A. W. Hofmann's *Introduction to Modern Chemistry, experimental and theoretic*, published in 1865, did a great deal to make clear the conception of the equivalency of atoms. Hofmann's treatment of the subject is so admirable that I make no apology for quoting somewhat fully from his book.[1]

[See table on upper part of p. 284.]

" . . . The atoms of the four central elements, chlorine, oxygen, nitrogen, and carbon, stand related respectively to 1, 2, 3, and 4 hydrogen-atoms. . . . It takes the whole atom-power of chlorine, 35·5, to engage 1 atom of hydrogen; whereas the atom-power of oxygen, 16, suffices to engage 2 hydrogen atoms; and the atom-powers of nitrogen and carbon suffice, respectively, to engage 3 and 4 hydrogen-atoms."

" . . . The table places before us the four centrally disposed elements, in two perfectly distinct chemical relations; the first more especially *volumetric* and *molecular*, the second essentially *numerical* and *atomic*. Hence, two parallel series of minimum weights; one representing the minimum quantity of each element requisite to take part in the formation of a compound *molecule*, the other corresponding to the minimum quantity of each element which is adequate to engage or fix one standard atom."

Hofmann then compares "these two sorts of chemical value, the *molecule-forming* and the *atom-fixing*," for hydrogen and chlorine, oxygen, nitrogen, and carbon, and tabulates his comparison thus. [Table on lower part of p. 234.]

---

[1] The quotations in the text are from Lecture X, pp. 163–186.

MOLECULAR AND ATOMIC CONSTITUTION OF THE FOUR TYPICAL COMPOUNDS.

Product-volumes = Molecules.   Unit-volumes = Atoms.

$$H\,Cl = 36\cdot5 \quad = \quad \boxed{Cl\ 35\cdot5} \ + \ \boxed{H}$$

$$H_2 O = 18 \quad = \quad \boxed{O\ 16} \ + \ \boxed{H} \ \ \boxed{H}$$

$$H_3 N = 17 \quad = \quad \boxed{N\ 14} \ + \ \boxed{H} \ \ \boxed{H} \ \ \boxed{H}$$

$$H_4 C = 16 \quad = \quad \boxed{C\ 12} \ + \ \boxed{H} \ \ \boxed{H} \ \ \boxed{H} \ \ \boxed{H}$$
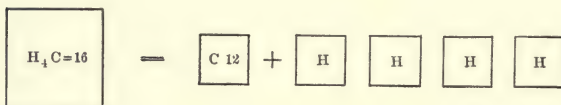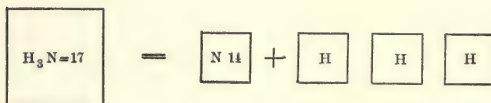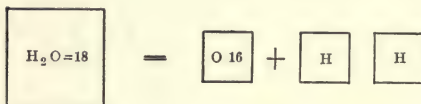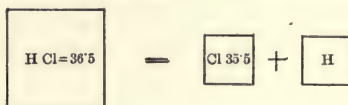
"CHEMICAL VALUES, MOLECULE-FORMING AND ATOM-FIXING, OF THE STAND-
ARD ELEMENT, HYDROGEN, AND OF THE FOUR TYPICAL ELEMENTS
WITH THE RATIOS OF THOSE VALUES.

The four typical elements preceded by the standard element, hydrogen.		Minimum weights thereof required		Ratios of the numbers in columns (3) and (4).
Their names. (1)	Their Literal symbols. (2)	To take part in the formation of a molecule. (3)	To engage one standard atom. (4)	(5)
Hydrogen.	H	1	1	$\dfrac{1}{1} = 1$
Chlorine.	Cl	35·5	35·5	$\dfrac{35\cdot5}{35\cdot5} = 1$
Oxygen.	O	16	8	$\dfrac{16}{8} = 2$
Nitrogen.	N	14	4·66	$\dfrac{14}{4\cdot66} = 3$
Carbon.	C	12	3	$\dfrac{12}{3} = 4$

" In this table . . . column 3 represents the *molecule-forming equivalents*
of the elements, or the proportions by weight in which they can replace each

other in contributing to the construction of a *molecule*; while column 4 sets forth the *atom-fixing equivalents* of the elements, or the proportions in which they can replace each other in fixing a standard atom." Hofmann says we might "attach to each element *two* representative or equivalent numbers; one expressing its minimum weight relatively to the formation of a *molecule*, the other its minimum weight relatively to the fixation of an *atom*."

But to do this would be inconvenient and burdensome. Both weights may be included in "a single concise expression," by attaching to each atomic weight (or, as Hofmann calls it, "molecule-forming minimum weight") "a coefficient of atom-fixing power; that is to say, a sign expressing how many standard atoms its said weight is adequate to satisfy." The ratios in the last column of the table are these coefficients.

"We are in want of a good appellation to denote the atom-fixing power of the elements. The vague and rather barbarous expression *atomicity* has drifted into use for this purpose; and the elements have been called *mon*atomic, *di*atomic, *tri*atomic, and *tetra*tomic. . . ." Hofmann regarded these names as misleading, because they seem to refer to the atomic structure of the molecules of the elements. He proposed to substitute *quantivalence* for *atomicity*, and "to designate the elements *uni*valent, *bi*valent, *ter*valent, and *quadri*valent, according to their respective atom-fixing values."

"The unequal *molecule-forming* powers of the elementary bodies . . . and their unequal *atom-fixing* powers . . . show us that each of these bodies possesses what may be termed its *specific chemical value in exchange*."

He then says that in "power of forming a molecule," 12 parts by weight of carbon are "worth" as much as 14 parts of nitrogen, as 16 of oxygen, or as 35·5 of chlorine; and that in power of fixing a standard atom, the elements in the four groups (the chlorine group, the oxygen group, the nitrogen group, and the carbon group) possess *chemical value in exchange* varying from 1 to 2, 3, and 4; or that "one atom of any element in group 4 is *exchangeable at par* for *four* atoms of any element in group 1," and so on.

"In learning," Hofmann says, "how many standard units of quantivalence any given elementary atom can attract and retain within a compound molecule, we learn also how many it can remove therefrom when it is employed as a decomposing agent."

Regarding the meaning of the term *quantivalence*, Hofmann says:

"This word is employed to designate the particular atom-compensating power inherent in each of the elements, and this power of theirs must by no

means be confounded with the specific *intensity* of their respective activities. Thus, for example, nitrogen, phosphorus, and arsenic are all of them *ter*valent bodies; but this equality of their atom-compensating values does not imply that they are all endowed with equal *avidity* for this or that element—say oxygen or hydrogen, for example."

Some of the applications of atomic equivalency to the classification of compounds were considered in the last chapter. In the next chapter we shall have other examples of these applications.

CHAPTER XI.

MOLECULAR STRUCTURE. ISOMERISM. CONSTITUTIONAL FORMULÆ.

THE experiments of Faraday,[1] in 1825, established the existence of two gaseous compounds "differing from each other in nothing but density." In 1830, Berzelius[2] proposed to use the word *isomeric* as a class-name for compounds which have the same composition, but different properties. He expressed the opinion that many instances of isomerism would be found.

In the preceding chapter we have seen that the experimental foundation of the study of chemical equivalency was laid by Richter towards the end of the eighteenth century; that the notion of equivalency was applied to the atoms of elements by Frankland in 1852; and that the idea of atomic equivalency was developed by Odling, Williamson, Cannizzaro, Kekulé, and Hofmann. In this chapter I propose to trace in some detail the development of atomic equivalency and the application of it to the classification of compounds, especially to compounds of carbon, and more especially to isomeric compounds, and to the formation of a language capable of setting forth the relations between the compositions, the properties, and the reactions of these compounds.

A great deal of work has been done on the subjects of isomerism and molecular structure. I shall direct the attention of the student only to those memoirs which seem to me to be of fundamental importance, and shall pass over unnoticed very many contributions which have helped to advance this part of the science of chemistry.

---

[1] *Phil. Trans.* for 1825, p. 440: *compare* Chapter VI, pp. 171, 172.
[2] *Pogg. Annal.*, **19**, 305: *compare* Chapter VI, p. 173.

In Chapter X I referred to a memoir by Couper [1] published in 1858. Couper showed that the combining power of an atom of carbon is expressed by the number four, and that "carbon enters into chemical union with itself." Taking the atomic weight of carbon to be 12, and that of oxygen to be 8, he gave to methylic and ethylic alcohols the formulæ

$$
\begin{array}{ccc}
\dots\dots O\dots\dots OH & & \dots O\dots OH \\
C\dots\dots H_3 & \text{and} & C\dots H_2 \\
& & \quad\cdot\;\cdot \\
& & \quad C\dots H_3
\end{array}
$$
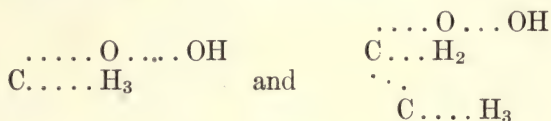
If the atomic weight of oxygen is 16, Couper's formulae become:

$$
\begin{array}{ccc}
\dots OH & & \dots OH \\
C\dots H_3 & \text{and} & C\dots H_2 \\
& & \quad\cdot\;\cdot \\
& & \quad C\dots H_3
\end{array}
$$
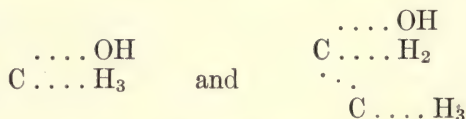
and these are the constitutional formulæ which are used to-day to express the reactions and relations of the two alcohols.

The formulæ used by Couper rested on the conception of the molecule as an orderly arrangement of atoms held together by actions and reactions between its parts; that conception has been the chief guide to the classification of compounds of carbon since Couper's time.

Couper's paper was published in the *Philosophical Magazine* for August, 1858. The March number of *Liebig's Annalen* of that year contained an extremely important memoir, by Kekulé, on the changes of chemical compounds and the chemical nature of carbon.[2] Kekulé arranged chemical changes under three headings. A chemical change is sometimes the direct addition of one molecule to another, and the formation of one new molecule; for instance, $NH_3 + HCl = NH_4Cl$, and $PCl_3 + Cl_2 = PCl_5$: sometimes several molecules are linked together by the agency of a poylatomic radical; for example,

[1] *Phil. Mag.* [4], **16**, p. 104.
[2] "Ueber die Constitution und die Metamorphosen der chemischen Verbindungen und über die chemische Natur des Kohlenstoffs," *Annal. Chem. Pharm.*, **106**, 129 [1858].
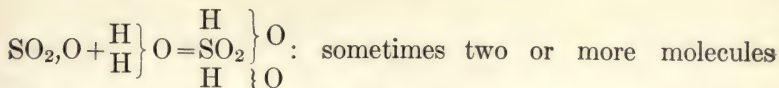
$$SO_2,O + \left.{H \atop H}\right\} O = {H \atop SO_2 \atop H}\left\}{\atop O \atop O}\right. :$$ sometimes two or more molecules
fall to pieces and their parts are re-arranged to form new molecules. When the parts of molecules are re-arranged—and most chemical changes belong to this class—equivalent quantities of elements or radicals are always exchanged.

In thinking of the decompositions and recompositions of molecules, Kekulé pictured to himself the formation of buildings constructed on definite plans. Kekulé was the greatest chemical architect the science has known; it is interesting to note that in early life he intended to devote himself to the profession of architecture.

In his speech to the German Chemical Society in 1890, on the occasion of the festival in his honour, Kekulé tells how he came to picture to himself the arrangements of atoms in molecules. He says:[1]

"During my stay in London [in 1854] I resided for a considerable time in Clapham Road in the neighbourhood of the Common. I frequently however spent my evenings with my friend Hugo Müller at Islington. . . . One fine summer evening I was returning by the last omnibus, outside as usual. . . . I fell into a reverie, and, lo, the atoms were gambolling before my eyes! Whenever, hitherto, these diminutive beings had appeared to me, they had always been in motion; but up to that time I had never been able to discern the nature of their motion. Now, however, I saw how, frequently, two smaller atoms united to form a pair; how a larger one embraced two smaller ones; how still larger ones kept hold of three or even four of the smaller; whilst the whole kept whirling in a giddy dance. I saw how the larger ones formed a chain, dragging the smaller ones after them, but only at the ends of the chain. . . . The cry of the conductor, 'Clapham Road,' awakened me from my dreaming; but I spent a part of the night in putting on paper at least sketches of these dream-forms. This was the origin of the *Structur-theorie*."

The following quotations from Kekulé's memoir of 1858 (p. 151 *onwards*) show the way in which he thought about and expressed the conception of the molecule as a building held together by the linking of its parts, which are atoms and groups of atoms.

"The radical of sulphuric acid, SO_2, contains three atoms, each of which is diatomic, and therefore represents two units of affinity. When the atoms

are linked, one unit of affinity of one atom enters into combination with one of another atom. Therefore four of the six units of affinity are used in holding together the three atoms; two remain over. Hence the group appears as diatomic; it combines, for example, with two atoms of a monatomic element:

<div style="display:flex; justify-content:space-around;">

Sulphuryl radical.

$$S'' \left\{ \begin{array}{l} O'' \\ O'' \end{array} \right.$$

Chlorosulphuric acid.

$$\begin{array}{l} Cl \\ S'' \\ Cl \end{array} \left\{ \begin{array}{l} O'' \\ O'' \end{array} \right.$$

</div>

"When chlorosulphuric acid reacts with water, 2HCl is given off; the other atoms remain combined, and the product (H_2SO_4) may be regarded as two molecules of H_2O in which two atoms of hydrogen are replaced by the group SO_2. A method similar to this may be used to represent the linkings of the atoms in all radicals, including those which contain carbon. It is only necessary to form a conception of the nature of carbon.

"If the simplest compounds of carbon are considered (marsh gas, methyl chloride, carbon chloride, chloroform, carbonic acid, phosgene gas, carbon sulphide, prussic acid, and so on), it is apparent that the quantity of carbon which chemists have recognized to be the smallest possible, the *atom*, always binds to itself four atoms of a monatomic element, or two atoms of a diatomic element; that the sum of the chemical units of the elements which are combined with one atom of carbon is always equal to four. This leads to the view that carbon is tetratomic (or tetrabasic). . . . In the cases of substances which contain several atoms of carbon, it must be supposed that at least some of the atoms are held in the compound by the affinity of the carbon, and that the carbon atoms are linked to one another, whereby, of course, a part of the affinity of one atom is bound by an equal part of the affinity of another atom. . . . The simplest and therefore most probable case of such linking of two atoms of carbon is that wherein one unit of affinity of one of the atoms is combined with one unit of affinity of the other atom. Two units, of the 2×4 units of affinity of the pair of atoms of carbon, are used in holding the two atoms together; six, therefore, are left, and can be bound by the atoms of other elements. In other words, a group of two atoms of carbon, C_2, will be hexatomic; it will form a compound by combining with six atoms of a monatomic element, or, in general, by combining with that number of atoms the sum of the chemical units whereof is equal to six. . . . If more than two atoms of carbon combine in the way we are considering, each additional atom will increase the basicity of the carbon-group by two units. The expression $n(4-2)+2=2n+2$ gives the number of atoms of hydrogen (chemical units) which will combine with n atoms of carbon united in the manner described. . . . So far we have supposed that all the atoms which are linked to carbon are held by the affinity of the carbon. We may, however, equally well suppose that only a part of the affinity of a polyatomic element (of O, N, etc.) is bound to carbon; only one of the two units of oxygen, or only one of the three units of nitrogen, for example, so that one of the two units of affinity of oxygen, or two of the three units of affinity of nitrogen remain unused and can be bound by other elements. The combination of these other elements with the carbon is therefore only indirect; this is indicated by writing the formulæ typically:

$$\left.\begin{array}{c} C_2H_5 \\ H \end{array}\right\}O \qquad \left.\begin{array}{c} C_2H_5 \\ H \\ H \end{array}\right\}N \qquad \left.\begin{array}{c} C_2H_3O \\ C_2H_5 \end{array}\right\}O \qquad \left.\begin{array}{c} C_2H_5 \\ C_2H_5 \\ C_2H_5 \end{array}\right\}N.$$
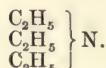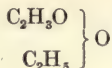
"Different carbon-groups are linked together by oxygen or by nitrogen. . . . The carbon-group appears as a radical; one says that the radical has replaced one atom of hydrogen of the type, because it has been able to saturate the affinity of the oxygen, or of the nitrogen, in place of the one atom of hydrogen. By comparing with one another compounds which contain equal numbers of atoms of carbon in their molecules, and are formed one from the other by simple metamorphoses (for instance, alcohol, ethylchloride, aldehyde, acetic acid, glycollic acid, oxalic acid, etc.), one arrives at the view that the atoms of carbon in these compounds are similarly linked, and the only atoms which change are those which are linked to the carbon-skeleton.

"An examination of homologous bodies leads to the view that the atoms of carbon in these compounds (whatever be the number of these atoms) are linked to one another in the same way, in accordance with the same law of symmetry.

"Such a 'simplest' linking of atoms of carbon may be assumed for very many organic compounds. So many atoms of carbon are present in the molecules of some compounds that a greater condensation of these atoms must be assumed in these compounds.

"Benzene, and all of its derivatives, for example, and also the hydrocarbons homologous with benzene, contain a much greater quantity of carbon than those compounds which are allied to ethyl, and this causes a characteristic difference between the two classes of compounds. As naphthalene contains yet more carbon, one must suppose that the carbon in this compound is more condensed even than in benzene, that is, the single atoms are more closely linked to one another. . . . There seem to be three classes of compounds which contain carbon, and these appear to be distinguished from one another by the nature of the linking of the atoms of carbon."

The chief ideas which Kekulé's memoir of 1858 enabled chemists to grasp and use as instruments of research were these.

A molecule is a building of atoms; each atom can be linked to a limited and definite number of others; in some molecules, every atom is linked to the greatest possible number of other atoms; in some molecules, some of the atoms are linked to less than the maximum number of others. An atom of carbon can be linked to four other atoms; when two atoms of carbon are joined together in the simplest possible way, the group of two atoms can link itself to six other atoms; a group of three simply linked atoms of carbon can be joined to eight other atoms, and so on. Many of the metamorphoses of compounds of carbon are substitutions of atoms, or groups of atoms, which are linked to atoms of carbon, by

equivalent quantities of other atoms or atomic groups; the groups of linked atoms of carbon remain unaffected in these changes. As it is permissible to think and to speak of all the stones in a building as joined together, although only those which touch one another are directly joined, so it is legitimate to think and to speak of direct and indirect union of the atoms which form a molecule. Those atoms between which others are interposed are indirectly united to one another; those are in direct union between which no other atoms intervene. If six atoms of carbon are linked in the simplest manner, the group C_6 can combine with $(2 \times 6) + 2 = 14$ atoms of hydrogen; inasmuch as the group C_6 is combined with only six atoms of hydrogen in the molecule of benzene (C_6H_6), it is necessary to suppose that the atoms of carbon are more closely held together in this molecule than the atoms of carbon in the molecule C_6H_{14}, and in other molecules allied thereto. If ten atoms of carbon were linked in the same manner as the atoms of carbon are joined in the molecule of benzene, the group C_{10} would combine with fourteen atoms of hydrogen; inasmuch as the group C_{10} is combined with only eight atoms of hydrogen in the molecule of naphthelene ($C_{10}H_8$), it is necessary to suppose that the atoms of carbon in this molecule are more closely linked than those in the molecule of benzene. There are, then, at least three different ways wherein atoms of carbon may be linked to one another in the molecules of compounds of that element.

I ask the student to note the use which Kekulé made of the expressions, "*units of affinity*," "*the chemical units of an element*," "*the combination, or binding of a unit of affinity of one atom with, or by a unit of affinity of another atom*," and other expressions like these. These phrases have given rise to great searchings of hearts.

By boldly and carefully applying the idea of atomic equivalency to the reactions of carbon compounds, Kekulé developed a system of classifying these compounds which he set forth in his famous *Lehrbuch der Organischen Chemie oder der Chemie der Kohlenstoffverbindungen*, the first volume of which was published in 1861 (the preface is dated May, 1859) and the second volume in 1866. Although the book has never been com-

pleted, the portion of it which was given to chemists sufficed to lay fairly and surely the foundations of systematic organic chemistry.

To attempt a description of Kekulé's classification of carbon compounds would be to travel far beyond the limits of this book. I ask the student to notice that the method of Kekulé, which was the amplification and the detailed application of the notion of molecular structure, used three ideas, the progress of which was traced in Chapter IX of this book, namely, the idea of substitution, the idea of radicals, and the idea of types. Kekulé thought of a radical as a group of atoms which remains unchanged throughout the characteristic reactions of a number of compounds. He says: [1]

"Radicals are not firmly closed atomic groups, but they are merely collocations of atoms placed near together which do not separate in certain reactions, but fall apart in other reactions. It depends on the nature of the associated atoms, and on the nature of the substance which acts upon the compound, whether an atomic group does or does not play the part of a radical, and whether it is a more or less stable radical."

Again, he says:

"Different radicals may be assumed, according as a reaction goes more or less deeply."

Hence he thought it legitimate to represent a compound as belonging to more than one type. Kekulé looked on a type as an atomic building, after the model of which other atomic buildings are constructed. He spoke of the molecule of water $\left.\begin{array}{c}H\\H\end{array}\right\}O$ as a structure wherein two monatomic atoms of hydrogen are held together by one diatomic atom of oxygen, and he arranged under the water-type compounds whose molecules are formed of two monatomic atoms, or two monatomic radicals, held together by one diatomic atom or group of atoms. And similarly with other types.

Since the early sixties of the nineteenth century, the three notes of organic chemistry have been *substitution, equivalency, types*. The words have not been used so much of late years, but the ideas which the words express, as these ideas are interpreted

---

[1] *Annal. Chem. Pharm.*, **106**, pp. 151, 152.

and illuminated by the theory of molecules and atoms, are the working tools of organic chemists.

In his speech, already quoted from, Kekulé said: [1]

"I was sitting, writing at my text-book; but the work did not progress; my thoughts were elsewhere. I turned my chair to the fire and dozed. Again the atoms were gambolling before my eyes. This time the smaller groups kept modestly in the background. My mental eye, rendered more acute by repeated visions of the kind, could now distinguish larger structures, of manifold conformation: long rows, sometimes more closely fitted together; all twining and twisting in snake-like motion. But look! What was that? One of the snakes had seized hold of its own tail, and the form whirled mockingly before my eyes. As if by a flash of lightning I awoke; and this time also I spent the rest of the night in working out the consequences of the hypothesis.

"Let us learn to dream; . . . then perhaps we shall find the truth: . . . but let us beware of publishing our dreams before they have been put to the proof by the waking understanding."

Thus began Kekulé's benzene-hypothesis.

The first account of his views on the structure of the molecule of benzene was published in 1865,[2] and in fuller detail in 1866.[3] After describing the chief characteristic reactions of benzene (C_6H_6) and of compounds derived from benzene, Kekulé proposes two hypotheses whereby the facts may be expressed in terms of the linking of atoms and the tetratomicity (or quadrivalency) of the atom of carbon.[4]

"FIRST HYPOTHESIS.—The six carbon-atoms of C_6H_6 are united in a perfectly symmetrical manner; one may assume that they form a perfectly symmetrical ring; the six hydrogen atoms are placed symmetrically not only with regard to the carbon, but they also take completely similar places in the atomic system (molecule); they are therefore equivalent. Benzene may, then, be represented by a hexagon the six angles of which are formed by atoms of hydrogen.
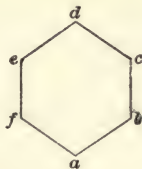
[1] Here, also, I quote from Japp's "Kekulé Memorial Lecture" in C. S. Journal, 73, 100 [1898].
[2] Bull. Soc. Chim., 1, 98 [January 27, 1865].
[3] Annal. Chem. Pharm., 137, 129 [February, 1866]: "Ueber die Constitution der aromatischen Verbindungen."
[4] Annal. Chem. Pharm., 137, 158–160 [1866].

" It is easily seen that the following are the possible isomeric modifications of derivatives formed by successive substitution; for bromine substitution-products, for example, we have:

(1) Monobromobenzene; one modification.
(2) Dibromobenzene; three modifications, *ab, ac, ad*.
(3) Tribromobenzene; three modifications, *abc, abd, ace*.
(4) Tetrabromobenzene; three modifications, as for (2).
(5) Pentabromobenzene; one modification.
(6) Hexabromobenzene; one modification."

"SECOND HYPOTHESIS.—The six atoms of carbon of benzene form three atomic groups, each of which consists of two atoms of carbon united by two units of affinity. The group appears as a triangle, and one may think of the carbon-atoms which form it as arranged so that three atoms of hydrogen are placed inside the triangle and three outside the triangle. The six atoms of hydrogen are not equivalent. . . . Three of the six atoms of hydrogen are placed at the angles, they are more easily accessible; the others are in the middles of the faces of the triangle, inside the molecule, so to say.
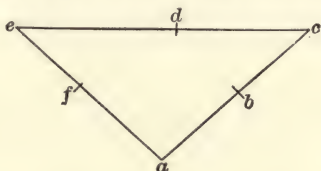
"The fact that benzene readily combines with one, two, or three molecules of chlorine or of bromine, but not with more, might perhaps be alleged in favour of this view; one might suppose that only the more accessible atoms of hydrogen are able to bring about such a combination. This conception evidently leads to the possibility of the existence of a much larger number of isomeric modifications, as is easily shown by the following examples.

(1) Monobromobenzene; two modifications, *a* and *b*.
(2) Dibromobenzene; four modifications, *ab, ac, bd, ad*.
(3) Tribromobenzene; six modifications, *abc, bcd, abd, abe, ace, bdf*."

How was the problem of the constitution of benzene to be solved?

Kekulé said:

" It is only necessary to prepare, by methods as varied as can be devised, as great a number of substitution-products of benzene as possible; to compare them very carefully with regard to isomerism; to count the observed modifications; and especially to endeavour to trace the cause of their differences to their modes of formation. When all this is done we shall be in a position to solve the problem."

Kekulé then discusses several substitution-products of benzene which were known when he wrote (in 1866), and pro-

nounces in favour of the hexagon-formula; at the same time he
indicates with perfect lucidity the investigations which should
be undertaken.

In 1867, Kekulé said [1] that no formula wherein the atoms
are represented as arranged in one plane could completely ex-
press the linkings of the atoms of carbon which he supposed to
exist in the molecule of benzene. He said that the shortcomings
would be removed if the [2]

"four units of affinity of the carbon-atom, instead of being placed in one
plane, radiate from the spheres representing the atoms in the direction of
hexahedral axes, so that they end in the faces of a tetrahedron. . . . A model
of this description permits of the union of 1, 2, and 3 units of affinity, and, it
seems to me, does all that a model can do."

The following figure is Kekulé's presentation of the arrange-
ment of the atoms in the molecule of benzene:
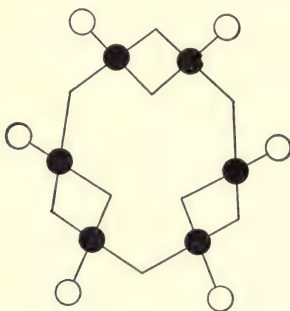
The black spheres represent atoms of carbon; the white spheres, atoms
of hydrogen. In the original, three methyl groups (CH_3) replace the three
hydrogen atoms, and the model represents the arrangement of the atoms
in the molecule of mesitylene (trimethylbenzene).

The 'units of affinity' of the atoms of carbon are repre-
sented in the model by wires of equal lengths; each of the six
atoms of carbon is supposed to be united to one carbon-atom by
a 'single bond' and to one carbon-atom by a 'double bond,'

---

[1] *Zeitsch. für Chemie* [2], **3**, 216 [1867].
[2] The words in the text are Japp's translation of the original (*C. S. Journal,*
73, 132 [1898]). A more elaborated model of the benzene molecule, by which all
the facts concerning the chemical and physical behaviour of benzene and its
derivatives may be expressed, is described by Sachse, *Zeitsch. für physikal. Chemie,*
10, 203 [1892].

and the model helps us to form mechanical conceptions of these expressions.

Because of its greater simplicity, and its direct applicability to most of the problems concerning the relations of derivatives of benzene, the hexagon-formula suggested by Kekulé in 1866 has been more used than the tridimensional formula, of which the figure given above is a partial representation.

It is not too much to say that all the great advances which have been made in the study of the derivatives of benzene since 1866 have been directly suggested by the results of Kekulé's dreams about the arrangements of atomic structures.   And although it is true that cases have been accumulated of late years of the co-existence of small differences of properties with identity of composition, which are not evidently provided for by the didimensional hexagon-formula of benzene, it is also true that these instances of the finest kind of isomerism have found, or are finding intelligible and suggestive expression in tridimensional formulæ which are based on Kekulé's image of carbon-atoms whose units of affinity terminate in the faces of tetrahedra.[1]

As Japp says [2] in his "Memorial Lecture":

"Kekulé's work stands pre-eminent as an example of the power of ideas. A formula consisting of a few chemical symbols jotted down on paper and joined together by lines . . . supplied work and inspiration for scientific organic chemists during an entire generation, and affords guidance to the most complex industry the world has yet seen."

In 1869, Brodie tried to laugh structural formulæ out of existence. [3]

"He found the works of Kekulé and Naquet scribbled over with pictures of molecules and atoms, arranged in all imaginable ways, for which no adequate reason was given; and if there was no reason for this, it was a mischievous thing to do, for it led to a confusion of ideas, and to mixing up fictions with facts."

It is so easy to make one's self believe that what one does not understand must be without reason, and what one supposes to be fiction cannot possibly be fact.

---

[1] The bearing of some determinations of physical properties on the formula of benzene will be historically discussed in Chapter XVI.
[2] C. S. Journal, 73, 138 [1898].
[3] Ibid., 22, 440 [1869]; report of the discussion on a paper by Williamson.

It would seem to follow from the quotations I have given from his memoirs of 1858 and 1866, that Kekulé regarded structural formulæ as expressions of the real arrangements of the parts of molecules. Let us hear what he himself said about these formulæ.[1]

"Rational formulæ are decomposition-formulæ, and in the present state of science can be nothing more. These formulæ give us pictures of the chemical nature of substances; because the manner of writing them indicates the atomic groups which remain unattacked in certain reactions (the radicals), or lays stress on the constituents which play the same part in definite, oft-recurring metamorphoses (types). Every formula which expresses definite metamorphoses of a compound is *rational*; that one of the different rational formulæ is the *most rational* which expresses the greatest number of metamorphoses."

It is instructive to compare Couper's view of rational formulæ with that of Kekulé. Couper said:[2]

"Gerhardt . . . is led to think it necessary to restrict chemical science to the arrangement of bodies according to their decompositions, and to deny the possibility of our comprehending their molecular constitution. Can such a view tend to the advancement of science? Would it not be only rational, in accepting this veto, to renounce chemical research altogether?"

Kekulé held that if the arrangement of atoms in molecules is ever understood, it will be by the study of physical properties rather than of chemical reactions. He thought it possible that one might thus attain to true *constitutional* formulæ.

Chemists do not now very strenuously dispute about the exact extent to which rational formulæ express "the molecular constitutions of bodies." These formulæ have proved themselves to be such powerful instruments of research that chemists are content to use them for the purpose in hand, without discussing what other purposes they may some day serve. The use of rational formulæ is a representative instance of the fruitful employment of hypotheses for the advancement of accurate knowledge.

Is the atomicity, the quantivalence, the valency of an atom fixed or variable? A vast amount of discussion has been given to this question.

---

[1] *Annal. Chem. Pharm.*, **106**, 149 [1858].
[2] *Phil. Mag.* [4], **16**, 107 [1858].

When Frankland enunciated the law of atomicity in 1852, he said that "the combining power of the attracting element is always satisfied by the same number of the uniting atoms." In the introductory remarks to Chapter V of his collected *Researches* (p. 145) Frankland says:

"The discovery of the law of variation in the atomicity of elements was made many years subsequenely [to 1852], and was announced for the first time in my *Lecture Notes for Chemical Students*, published in September, 1866, as follows: 'This variation in atomicity always takes place by the disappearance or development of an even number of bonds: thus, nitrogen is either a pentad, a triad, or a monad; phosphorus and arsenic, either pentads or triads; carbon and tin, either tetrads or dyads; and sulphur, selenium, and tellurium, either hexads, tetrads, or dyads. These remarkable facts can be explained by a very simple and obvious assumption, viz., that one or more pairs of bonds belonging to an atom of the same element can unite, and, having saturated each other, become, as it were, latent.' "

In 1864, Frankland thought that each atom has a fixed maximum combining power, but that the whole of this power is not always used.

A discussion on the fixity or variability of atomic equivalency was carried on by Kekulé, Wurtz, Naquet, and Williamson in 1864.[1] Kekulé insisted that "the atomicity is a fundamental property of the atoms, which is as constant and unchangeable as the atomic weight itself." "The equivalent [of an element] may vary," he said, "but the atomicity cannot; on the contrary, the variation of the equivalent must be explained by the atomicity." Naquet and Wurtz held that the atomicities of some elements vary in the compounds of these elements. If, however, the atomicity of an element means its maximum saturation-capacity, Naquet admitted that this property is unchangeable.

The discussion really turned on the meaning to be given to the words *atomicity* and *atomic equivalency*. Kekulé expressed the facts that one atom of carbon combines with four atoms of hydrogen, and one atom of oxygen combines with two atoms of hydrogen, by saying that an atom of carbon has four units of affinity and an atom of oxygen has two units of affinity. An

[1] Papers were published in *Bull. Soc. Chim.* and in *Compt. rendus*; German translations appeared in *Zeitsch. für Chemie*, **7**, 679–702 [1864].

atom of carbon, Kukelé said, has always four units of affinity, and an atom of oxygen has always two units of affinity; neither atom has ever more or less than these numbers of units of affinity. When an atom of carbon unites with two atoms of oxygen, the four units of affinity of the former atom are satisfied, or saturated, by the four units of affinity of the two oxygen-atoms. And so in other cases. The existence of the molecule CO of course made it necessary to admit that the whole of the units of affinity of an atom are not necessarily saturated in all its compounds. Kekulé asserted that, in all stable and definite compounds, "the affinity-units of one atom are wholly or partially saturated by an equal number of affinities of another atom, or of several other atoms."

But what are 'stable and definite compounds'? Kekulé proposed to distinguish between *atomic* and *molecular* compounds. He said: "Those compounds all the elements of which are held together by affinities that mutually saturate one another may be called atomic compounds. These are the true chemical molecules, and these only can exist in the state of gas." Chemical action is always preceded, Kekulé taught, by the coming together of different molecules; if double decomposition—that is, exchange of atoms—cannot happen, because of the nature of the atoms, the attracted molecules may form groups which are much less stable than atomic compounds, and cannot be gasified without decomposition. Such groups of molecules were called molecular compounds by Kekulé. As examples of molecular compounds, Kekulé cites PCl_3,Cl_2; NH_3,HCl; $SeCl_2,Cl_2$; ICl,Cl_2, and others.

The discussion concerning variable or fixed valency changed to a discussion concerning atomic and molecular compounds. Many chemists admitted a distinction between what Kekulé called atomic and molecular compounds, but declared Kekulé's criterion to be too vague. Decomposition by heat is the mark of a molecular compound: at what temperature must the decomposition begin? Water-gas is admitted to be an atomic compound; but water-gas separates into hydrogen and oxygen at a very high temperature; is it to be classed as a molecular compound at one temperature and an atomic com-

pound at another temperature? Naquet tried to define atomic compounds to be those which react in double decompositions, but the description broke down in practice. The discussions about varying valency and atomic and molecular compounds gradually subsided. They were provocative of many researches, and therein they were fruitful.

Frankland, in 1866, spoke of the "simple and obvious assumption, that one or more pairs of bonds belonging to an atom of the same element can unite, and, having saturated each other, become, as it were, latent." Kekulé, in 1864, said that "those compounds all the elements of which are held together by affinities that mutually saturate one another may be called atomic compounds." Most of the discussions regarding atomic and molecular compounds, and fixed or varying valency, were attempts to form definite physical images of 'bonds,' 'pairs of bonds saturating each other,' and 'atoms held together by affinities that mutually satisfy one another.'

The instrument fashioned by Frankland and polished by Kekulé had done, and was doing valuable service; those who were using it wished to see of what it was made and how it was constructed. Memoirs and text-books published from the sixties to the early nineties of last century are full of critical and historical discussions of *bonds* and *units of affinity*. The rapid development of physical chemistry, and especially the growth of the ionization theory, have shifted the centre of chemical interest for a time. Moreover, the extraordinary richness of the results which have been obtained by using the conceptions of atomic equivalency and atomic linking as aids to classification have diverted the attention of chemists from the phraseology in which these conceptions have been expressed.

I ask the student's attention for a few minutes to a critical memoir on the subject of the arrangement of atoms in molecules, by W. Lossen, published in 1880.[1]

Lossen attempted to give more precise meanings than others had given to the terms used by chemists to express their ideas concerning molecular structure.

---

[1] "Ueber der Vertheilung der Atome in der Molekel," *Annal. Chem. Pharm.*, **204**, 265 [1880].

He said that the notions of atomic equivalency and atomic linking should be applied in detail only to those compounds the molecular weights of which have been determined by the use of Avogadro's hypothesis. Lossen spoke of an atom in direct union with another as being in the zone of union (*Bindungszone*) of the other atom, and said that, so far as we know, six is the greatest number of atoms which can be in the zone of union of any single atom.

Having defined the atoms of hydrogen, fluorine, chlorine, bromine, iodine, and thallium to be *univalent*, because "all [gaseous] molecules which contain only these elements consist of two atoms," Lossen said: "Hence none of these atoms is able to bind, *at the same time, two* atoms of the same category; none can bring about *indirect* combination between two such atoms." As regards multivalent atoms, Lossen said:

"The number of atoms which can be directly bound to a single atom of an element is constant for univalent atoms, but is variable for multivalent atoms, in which it increases to a maximum number. . . . The valencies of the atoms which are directly bound to a multivalent atom vary much. In the molecule CH_4 four univalent atoms are found in the zone of union of a quadrivalent atom of carbon; four bivalent atoms are found in the same zone of union in the molecule $C(OC_2H_5)_4$; in the molecule $C(CH_3)_4$ there are four quadrivalent atoms in the zone of union of one atom of carbon; and this atom directly holds two univalent atoms, one tervalent atom, and one quadrivalent atom in the molecule $H_2C{<}{\begin{smallmatrix}CH_3\\NH_2\end{smallmatrix}}$. The valency of an atom can therefore be found from the number of atoms which are directly bound to it, independently of the valencies of those atoms."

The valency of an atom was defined by Lossen to be a number which tells how many atoms are in direct union with it. According to Lossen, the valency of a multivalent atom is variable, but has a maximum or limiting value which is determined by experiment. If this maximum value is spoken of as the valency of the atom, then, of course, the valency of every atom has a constant value. The word *valency*, Lossen said, was commonly used in two meanings; sometimes it meant the maximum valency of an atom, sometimes the actual valency of that atom in this or that molecule. If it is said, 'the atom of carbon is bivalent or tervalent,' to complete the meaning one must add, 'in this or that determinate molecule': if one says only,

'the atom of carbon is quadrivalent,' one means that four is the maximum valency of that atom, that an atom of carbon never binds to itself more than four other atoms. According to Lossen, the linkings of the atoms of carbon in the molecule of acetylene are completely defined by the statement, 'the molecule C_2H_2 contains two bivalent carbon-atoms.' Similarly, to say that 'the molecule of benzene contains six tervalent carbon-atoms, each of which is linked to an atom of hydrogen,' gives as complete a description of the linkings of the atoms in the molecule C_6H_6 as the facts warrant. The formulæ generally given to ethylene (C_2H_4), acetylene (C_2H_2), and acetic aldehyde (C_2H_4O) were these:

$$\begin{matrix} H \\ \diagdown \\ H \diagup \end{matrix} C = C \begin{matrix} H \\ \diagup \\ \diagdown H \end{matrix}, \quad H-C \equiv C-H, \quad \text{and} \quad \begin{matrix} H \\ \diagdown \\ H \diagup \end{matrix} H-C-C \begin{matrix} O \\ \diagup \\ \diagdown H \end{matrix}.$$

Lossen used the formulæ:

$$\begin{matrix} H \\ \diagdown \\ H \diagup \end{matrix} C-C \begin{matrix} H \\ \diagup \\ \diagdown H \end{matrix}, \quad H-C-C-H, \quad \text{and} \quad \begin{matrix} H \\ \diagdown \\ H \diagup \end{matrix} H-C-C \begin{matrix} O \\ \diagup \\ \diagdown H \end{matrix}.$$
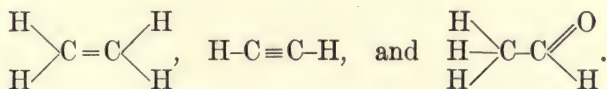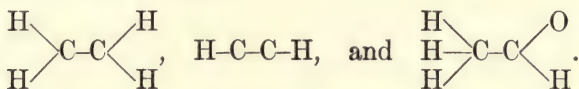
He admitted that his formulæ implied less than those in ordinary use, but he asserted his formulæ to be expressions of "all we can take to be fairly certainly established concerning the distributions of the atoms in the molecules."

Lossen dealt with the valencies of radicals in the same way as he dealt with the valencies of elementary atoms. "The valency of a radical," he said, "is a number which expresses how many atoms, not belonging to the radical, are directly bound to the atoms which compose the radical." As with atoms, so with radicals, there is a limiting value for the valency of each, but the actual valency in determinate compounds is often less than the limiting value. Lossen described a radical as "an atomic complex, contained in a molecule, all the constituents of which are linked either directly or indirectly." He said: "Every such part of a molecule may be called a radical; but, as a rule, only those atomic aggregates are called radicals which have the character just described and are present in a large number of molecules."

When Lossen's memoir appeared, in 1880, it was customary to deduce the valency of an atom by considering not only the number, but also the valencies of the atoms directly bound to it in various molecules; an atom was said to be n-valent when n is the sum of the valencies of the atoms which the specified atom directly binds to itself in any molecule. Lossen said that this method of procedure assumed mutual actions between indefinable somethings called *units of affinity*, or *bonds*, or *valencies*, and was not based solely on the conception of actions or reactions between atoms. Kolbe [1] had spoken of half the affinity of the quadrivalent atom of carbon as 'slumbering' in the molecule of carbon moxonide. Lossen remarked,[2] "What is not, slumbers not, and what slumbers is also there." He could see no real difference between Kolbe's 'slumbering affinities' and Kekulé's statement that the atom of carbon in the molecule CO acts with only two affinity-units on the two units of affinity of the oxygen-atom, and two affinity-units of carbon remain 'free' or 'unsatisfied,' or, as Frankland said, 'latent.' Molecules which contained 'free affinities' were supposed to combine very readily with other molecules. The combination of carbon monoxide and chlorine was generally expressed thus:

$$O = C = + Cl - Cl = O = C = Cl_2.$$
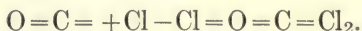
It was supposed that the two 'free affinities' of the carbon-atom were eager to be 'satisfied' by the affinities of the atoms of chlorine. Lossen said that reactions like this are not peculiar to molecules with 'free affinities'; for instance, the reaction $C_2H_4 + Br_2 = C_2H_4Br_2$ goes rapidly, but the molecule C_2H_4 is not supposed to contain any 'free affinities.' It is just as correct to say that the molecule Cl_2 is very ready to combine with CO, as to say that the latter molecule is peculiarly eager to combine with the former.

Lossen arranged in three groups the hypotheses concerning the valencies of atoms which had been promulgated by chemists of authority before 1880. There were, he said, those hypotheses

---

[1] *J. prakt. Chem.* [2], **19**, 486 [1879].

[2] "Was nicht ist, das schlummert auch nicht, und was schlummert, das ist auch da."

which regarded 'an affinity' as an action of some kind associated with a quantity of an element different from the atomic weight of it. There were those hypotheses which regarded 'an affinity' as a part of an atom, or, perhaps, something connected with a part of an atom. There were those which regarded 'an affinity' as a form of motion of an atom.

The most prominent of the hypotheses belonging to the first of Lossen's classes was that developed by Erlenmeyer,[1] who spoke of *affinivalencies*, or the constant masses of elements which, he asserted, attract one another in all compounds, and said that one affinivalency of an element never binds to itself more, and never less, than one affinivalency of another element. The affinivalencies of carbon and oxygen were taken by Erlenmeyer to be 3 and 8 respectively. But, Lossen remarked, if an affinivalency of carbon binds to itself one of oxygen in the molecule CO_2, it follows that an affinivalency of carbon binds only half an affinivalency of oxygen in the molecule CO.

Lossen criticised in detail the various forms which had been given (by Hofmann, Lothar Meyer, Butlerow, and others) to the hypothesis that affinities are actions proceeding from equivalent weights of elements. He found them all vitiated by failure to mark the distinction between atomic weights and equivalent weights. Atoms attract one another; equivalent weights are merely imagined sums, or fractions, of the masses which act and react in molecules.

Lossen's general criticism of the second hypothesis—an affinity is something connected with a part of an atom—was, that this predicates qualitative differences between the parts of atoms, and introduces a conception of the atom which differs entirely from that generally used by chemists, and is too vague to be of service.

The third hypothesis—'an affinity' is a form of motion of an atom—had been tentatively proposed by Kekulé, and used in a vague way by Lothar Meyer. The forms which this hypothesis had taken were thought by Lossen to be too indefinite for detailed criticism.

---

[1] *Lehrbuch der Organischen Chemie*, p. 39 [1867].

Finally, as regards the meaning of structural or rational formulæ, Lossen regarded as only partially correct the view of Kekulé that the positions of atoms in space cannot be ascertained by studying chemical metamorphoses, but, if at all, only by comparative investigations of the physical properties of compounds.

"The study of physical properties," Lossen said, "will certainly be the primary method of learning something about the absolute positions of atoms. The relative positions of atoms . . . can be elucidated by the study of chemical metamorphoses, because these are dependent on those positions." And again: "The *action* of a determinate atom on the other atoms in the same molecule depends on the relative position of the atom in question; *the proportions* and *the chemical behaviour* of the molecule depend on *the actions of all the atoms* on one another. Therefore, unquestionably, observations of *the properties and the behaviour of a substance* enable us to draw conclusions concerning *the mutual actions of the atoms in the molecule of that substance*, and concerning *the positions of the atoms relatively to one another*."

Notwithstanding the vagueness of the expressions 'bonds,' 'affinities,' 'free affinities,' 'satisfaction of units of affinity,' and the like, chemists continue to use rational formulæ wherein the numbers of lines which proceed from the atomic symbols express the maximum valencies of the atoms, and in many cases do not express their actual valencies in the molecules formulated; they continue to speak of 'single,' 'double,' and 'treble linkings of atoms,' 'loosening and breaking of double bonds,' 'change of a single to a double linking,' etc., and they sometimes discuss whether all the bonds of an atom are of equal value or equal strength.[1] These phrases, and others like them, have been retained because they have proved to be convenient general expressions of reactions. The interactions of compounds of carbon find expression in terms of atomic equivalency and atomic linkings only when it is recognized that atoms of carbon can be linked in different ways. Lossen's formulæ for ethane, ethylene, and acetylene, for example,

_____
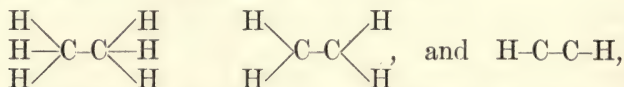
[1] For an account of certain discussions about the thermal values and the spectrometric values of different kinds of linkings of carbon atoms, see Chapter XVI.

do not visually emphasize the existence of differences between the interactions of the two carbon-atoms in these molecules. Whatever meanings are given to the expressions 'single bonds,' 'double bonds,' and 'treble bonds,' there is no doubt that the structural formulæ commonly used for ethane, ethylene, and acetylene make patent to the eye that the linkings, that is to say, the mutual actions of a pair of carbon-atoms are not the same in these three molecules. The formulæ in question are these:

$$\begin{array}{c}H \\ H \\ H\end{array}\!\!\diagdown C\!-\!C\!\diagdown\!\!\begin{array}{c}H \\ H \\ H\end{array} \qquad \begin{array}{c}H \\ H\end{array}\!\!\diagdown C = C\!\diagdown\!\!\begin{array}{c}H \\ H\end{array}, \quad \text{and} \quad H\!-\!C\!\equiv\!C\!-\!H.$$
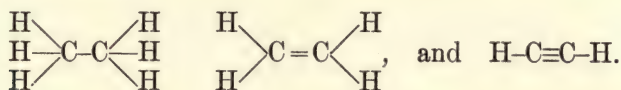
The vagueness of the expressions used to describe atomic interactions is one reason why these expressions have continued to be employed: chemistry is only feeling its way towards definite ideas about molecular structure. One cannot, however, but regret that the word *affinity* should have been used, should be used in an extraordinarily loose manner in discussions about the linkings of atoms.

The investigation of isomerism was greatly advanced by the publication of two memoirs in 1874.

In 1867, Kekulé suggested that the most satisfactory way of thinking about the structure of the molecule of benzene would be to suppose [1] that the four units of affinity of each atom of carbon "radiate from . . . the atom in the direction of hexahedral axes, so that they end in the faces of a tetrahedron."

The conception of the tetrahedral arrangement of an atom of carbon and four other atoms, or atomic groups, combined with it, was made a working hypothesis by Le Bel, and by van't Hoff, independently, in the year 1874. The memoir by van't Hoff was published in September, and Le Bel's memoir in November, of that year.[2]

A small book was published by van't Hoff in May, 1875,

---

[1] Compare this chapter, p. 296.
[2] Van't Hoff: "Sur les formules de Structures dans l' Espace," *Archiv. néerland*, **9**, 445 [1874]. Le Bel: "Sur les relations qui existent entre les formules atomiques des corps organiques et la pouvoir de leurs dissolutions," *Bull. Soc. Chim.* [2], **22**, 337 [1874].

entitled *La chimie dans l'Espace*.   A second and much enlarged
edition appeared in 1887, with the title *Dix Années dans l'his-
toire d'une Théorie*.   An English edition, *Chemistry in Space*,
appeared in 1891.   A freely revised version was published in
1894, and an English translation thereof, entitled *The Arrange-
ment of Atoms in Space*, appeared in 1898.

The light which is reflected from the surface of an object is
said to be *polarized;* it differs in several respects from the light
which comes from a luminous body.   The plane which contains
the incident ray and the normal to the reflecting surface is called
the plane of polarization.   Some substances turn the plane of
polarization of a ray of light to the right hand, some to the left
hand, and some do not cause any rotation.   Those substances
which rotate the plane of polarization are classed together as
optically active.

Crystalline quartz rotates the plane of polarization of a ray
of light; amorphous quartz is optically inactive.   Crystallized
sugar is inactive; melted sugar and a solution of sugar are
optically active.   Hence the optical activity of sugar is asso-
ciated with the structure of the molecules of that compound;
but the activity of quartz accompanies the crystalline aggrega-
tion of its particles.

A crystal is a definite structure from which various forms
can be obtained by modifying identical parts in the same manner
and at the same time.   Sometimes only half of the identical
parts are modified; the result is a *hemihedral* (half-developed)
form of the crystal.   The hemihedral form is enclosed by half
the number of faces which enclose the parent-form.   A regular
octahedron, for example, is enclosed by eight faces which meet
three rectangular axes at equal distances from the point of
intersection; but four such faces can form a closed figure which
is the regular tetrahedron; the latter is a hemihedral form of
the regular octahedron.   In some cases, two hemihedral forms
may be produced which are identical and superposable the one
on the other; in other cases, two hemihedral forms are pro-
duced which are one the opposite of the other and are not super-
posable.   Two *enantiomorphous* ('εναντιός = opposite) forms of
quartz have been known for many years; one of them rotates

the plane of polarization of a ray of light to the left hand, the other shows right-handed rotation.

The foregoing paragraphs contain a very brief outline of the chief facts concerning the connexions between composition, crystalline form, and optical activity which were known when Pasteur [1] began his investigations of these subjects in the year 1848.

Pasteur repeated the examination which had been made by de la Provostaye of the crystalline forms of the tartrates. He noticed the fact, overlooked by his predecessor, that the tartrates "gave undoubted evidence of hemihedral faces." As solutions of the tartrates were known to be optically active, Pasteur thought that "there might be a relation between the hemihedry of the tartrates and their property of deviating the plane of polarization of light." He then proved that many crystallizable organic compounds which are optically active show hemihedry; and that racemic acid and its salts, which are isomeric with tartaric acid and its salts, but are optically inactive, do not show hemihedry. Pasteur tells us he was much disturbed by an observation made by Mitscherlich in 1844, that sodium-ammonium tartrate is identical, not only in composition but also in many physical properties, including crystalline form, with sodium-ammonium paratartrate (racemate), and that a solution of the former salt is optically active, while a solution of the latter is inactive. Mitscherlich said: "The nature and number of the atoms, their arrangement and distances, are the same in the two substances compared." Pasteur suspected that the double tartrate would show hemihedry, and that all the crystals of the double paratartrate would be absolutely identical. He prepared and examined crystals of both salts: the tartrate showed hemihedry; "but, strange to say, the paratartrate was hemihedral also. Only, the hemihedral faces, which in the tartrate were all turned the same way, were, in the paratartrate, inclined

[1] In 1860 Pasteur gave an account of his researches in two lectures delivered to the Chemical Society of Paris: "Recherches sur la dissymétrie moléculaire des produits organiques naturels. Leçons de Chimie professées en *1860*.' Paris [1861]. No. 14 of the *Alembic Club Reprints* is an English translation of these lectures; it is entitled "Researches on the molecular Asymmetry of natural organic products." Edinburgh [1897]. The quotations in the text are from that translation.

sometimes to the right and sometimes to the left." He separated the crystals which were hemihedral to the right from those hemihedral to the left, and examined solutions of each.

"I then saw, with no less surprise than pleasure, that the crystals hemihedral to the right deviated the plane of polarization to the right, and that those hemihedral to the left deviated it to the left; and when I took an equal weight of each of the two kinds of crystals, the mixed solution was indifferent towards the light in consequence of the neutralization of the two equal and opposite individual deviations."

Mitscherlich had proved the crystals of sodium-ammonium paratartrate to be isomorphous with those of sodium-ammonium tartrate; Pasteur showed that two kinds of crystals of the paratartrate are formed, and that therefore three sets of isomorphous crystals must be recognized.

"But," Pasteur said, "the isomorphism presents itself with a hitherto unobserved peculiarity: it is the isomorphism of an assymetric crystal with its mirror-image. This comparison expresses the fact very exactly. Indeed, if, in a crystal of each kind, I imagine the hemihedral facets produced till they meet, I obtain two symmetrical tetrahedra, which are inverse and cannot be superposed, in spite of the perfect identity of all their respective parts. From this I was justified in concluding that, by the crystallization of the double paratartrate of soda and ammonium, I had separated two symmetrically isomorphous atomic groups, which are intimately united in paratartaric acid. Nothing is easier than to show that these two species of crystals represent two distinct salts from which two different acids can be extracted."

Pasteur prepared the two acids. He found one to be identical with ordinary tartaric acid and dextrorotatory in solution, and the other to be lævorotatory in exactly the same degree as the first was dextrorotatory: he obtained "identical, but not superposable products; products which resemble each other like the right and left hands." By mixing concentrated aqueous solutions of equal weights of the two acids, Pasteur obtained crystals of inactive paratartaric (racemic) acid.

A study of the forms and the repetitions of identical parts of substances enables us, Pasteur said, to divide them all into two classes; those whose mirror-images are superposable, and those whose images are not superposable on the originals.

"A straight stair, a branch with leaves in double row, a cube, the human body—these are of the former class. A winding stair, a branch with the leaves arranged spirally, a screw, a hand, an irregular tetrahedron—these

are so many forms of the other set. The latter have no plane of symmetry. . . . All chemical compounds without exception likewise fall into two classes—those with superposable images and those with non-superposable images . . . bodies with asymmetric atomic arrangement and those with holohedral atomic arrangement." . . . "Each asymmetric substance offers four varieties, or, better, four distinct subspecies,—the right body, the left body, the combination of the right and the left, and the substance which is neither right nor left nor formed by the combination of the right and the left."

Crystalline quartz is optically active and hemihedral; amorphous quartz is inactive; therefore, Pasteur said, quartz is not *molecularly* asymmetric. As an aid to realizing the difference between molecular asymmetry and asymmetry due to crystalline structure, Pasteur used the image of a spiral stair.

"Imagine a spiral stair whose steps are cubes, or any other objects with superposable images. Destroy the stair and the asymmetry will have vanished. The asymmetry of the stair was simply the result of the mode of arrangement of the component steps. Such is quartz. The crystal of quartz is the stair complete. It is hemihedral. It acts on polarized light in virtue of this. But let the crystal be dissolved, fused, or have its physical structure destroyed in any way, its asymmetry is suppressed, and with it all action on polarized light, as would be the case, for example, with a solution of alum, a liquid formed of molecules of cubic structure distributed without order.

"Imagine . . . the same spiral stair to be constructed with irregular tetrahedra for steps. Destroy the stair, the asymmetry will still exist, since it is a question of a collection of tetrahedra. They may occupy any position, yet each will none the less have an asymmetry of its own. Such are the organic substances in which all the molecules have an asymmetry of their own, betraying itself in the form of the crystal. When the crystal is destroyed by solution, there results a liquid active towards polarized light, because it is formed of molecules, without arrangement it is true, but each having an asymmetry in the same sense if not of the same intensity in all directions."

As regards the mechanism of molecular asymmetry, Pasteur said:

"We know, on the one hand, that the molecular structures of the two tartaric acids are asymmetric, and, on the other, that they are rigorously the same, with the sole difference of showing asymmetry in opposite senses. Are the atoms of the right acid grouped on the spirals of a dextrogyrate helix, or placed at the summits of an irregular tetrahedron, or disposed according to some other particular asymmetric grouping? We cannot answer these questions."

Pasteur thought he had found in molecular asymmetry a peculiar mark of "products formed under the influence of life";

molecular asymmetry is absent, he said, from "all the products of inorganic nature." Here is another example of the drawing of boundary-lines which do not exist in nature. Since 1860, many molecularly asymmetric compounds have been formed in the laboratory.

In his second lecture, Pasteur describes various methods of separating many inactive organic compounds found in living organisms into two optically active isomerides, one dextrorotatory and the other lævorotatory.

The next very important step forwards in the investigation of molecular asymmetry was made in 1894 by Le Bel and by van't Hoff, independently.[1]

Le Bel started from the work of Pasteur, and used geometrical methods to gain exact conceptions of the orientation of the atoms in asymmetric molecules. The work of Kekulé on the quadrivalence of the carbon-atom was the point from which van't Hoff started in his attempt to correlate the optical activity of certain organic compounds with the spatial arrangement of the parts of the molecules of these compounds.

Le Bel and van't Hoff arrived at the same conclusions. When an atom of carbon is in direct union with four different atoms, or atomic groups, the arrangement is asymmetric; the molecules of optically active organic compounds contain at least one *asymmetric carbon-atom;* the atomic arrangement $CR_1R_2R_3R_4$, where R_1, R_2, R_3, and R_4 are different univalent atoms or groups of atoms, is to be thought of as a tetrahedron with the atom of carbon in its centre, and the four different atoms, or radicals, at the four summits; this tetrahedral arrangement is not superposable on its mirror-image; and, if one of the arrangements is associated with right-handed optical activity, the other *geometrical isomeride,* or *mirror-isomeride,* will rotate the plane of polarization of a ray of light to the left hand.

The hypothesis of the asymmetric carbon-atom has been very fruitful. It has suggested large fields of inquiry, and has provided means for their profitable cultivation.

The optical activity of compounds has been predicted from

[1] For references, see foot-note to p. 307.

a knowledge of their chemical reactions and relations. Several compounds have been proved to be optically inactive which had been classed among active substances, although their chemical relations were expressed by formulæ that contained no asymmetric atoms of carbon. Compounds which do not contain asymmetric carbon are inactive although they may be derived from others which rotate the plane of polarization of a ray of light.

Many compounds whose reactions are expressed by formulæ which contain asymmetric carbon-atoms have been proved to be optically inactive. Some of them have been divided, or resolved, into equal weights of two isomerides, one dextrorotatory, the other lævorotatory. Others have not been divided; they belong to an inactive, indivisible type the existence of which is predicted by the hypothesis.

Pasteur said:

"Each asymmetric substance offers four varieties, or, better, four distinct subspecies—the right body, the left body, the combination of the right and the left, and the substance which is neither right nor left, nor formed by the combination of the right and the left."

The reactions and relations of each of the four varieties of tartaric acid are expressed by the formula,
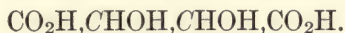
$$CO_2H, CHOH, CHOH, CO_2H.$$

The carbon-atoms represented by italicized C in the formula are asymmetric; each is in direct union with four different atoms or atomic groups, namely, H, OH, $CHOHCO_2H$, and CO_2H. If a molecule which has this composition is represented by a pair of tetrahedra with two summits in common, and these different arrangements are projected on to a plane surface, we have the following expressions:

I.	II.	III.	IV.
CO_2H	CO_2H	CO_2H	CO_2H
HOCH	HCOH	HCOH	HOCH
HCOH	HOCH	HCOH	HOCH
CO_2H	CO_2H	CO_2H	CO_2H

If IV is turned upside down, by rotating it through 180° in the direction wherein the hands of a watch move, it becomes

III; these two formulæ are therefore the same. The configuration represented by formula III, or by IV, is symmetrical; each half of the molecule is asymmetrical, but the asymmetry of either half is compensated by that of the other half. Configuration III or IV represents the inactive and indivisible tartaric acid: it is inactive, because the molecule is symmetrical; it is indivisible, because separation of the molecule into two parts means the destruction of the acid. The acids represented by formulæ I and II are asymmetric: if I represents the dextrorotatory acid, the lævorotatory acid is represented by II. A combination of equal numbers of molecules I and II must be inactive, but separable into equal weights of the right-handed and the left-handed isomerides; this is racemic acid (called by Pasteur paratartaric acid). In racemic acid we have, as Pasteur said, "a double molecular asymmetry concealed by the neutralization of opposite asymmetries, the physical and geometrical effects of which rigorously compensate each other." Pasteur said that chemical language wanted a word to express this double, concealed asymmetry; he suggested that compounds of this class are "perhaps like paratartaric acid." The word has been found; Pasteur's suggestion has been followed. Compounds which are *inactive by external compensation*, that is, are formed by the union of equal numbers of dextrorotatory and lævorotatory molecules and are separable into equal weights of two oppositely active isomerides, are called *racemic compounds*.

The fundamental idea of the work done by van't Hoff, and by Le Bel, is, that *the molecule is a stable system of material points*. In the first chapter of *The Arrangement of Atoms in Space* van't Hoff said:

"One might suppose that the arrangement of the atoms in the molecule would be something like that in a system of planets, equilibrium being maintained by attraction and motion. . . . I will try to show that we must exclude this motion . . . as a necessary consequence of simple thermodynamic considerations. . . . The internal stability of the molecule is attained only at absolute zero, that is, in the absence of all internal motion. Otherwise interaction with another molecule is an essential condition of the equilibrium. . . . The state of things at absolute zero is to be explained solely by atomic mechanics. . . . For stereochemistry . . . the motion of the atoms may for the present be neglected, the state of things being tacitly

assumed to be as it would be at absolute zero. Indeed, the phenomena of isomerism are in a certain sense opposed to motion; they are certainly not a consequence thereof; for when the temperature rises they ultimately disappear, and become constantly more marked as it falls. He who chooses to assume motion, however, may conceive the motionless systems here to be described as the expression of the position of certain points about which the motion, doubtless a periodical motion, takes place."

Applying this conception of the molecule, as a stable system of material points, to the isomerism of compounds which contain "doubly linked" atoms of carbon, and, of course, using the idea of tetrahedral arrangement, van't Hoff concluded that in these molecules, which belong to the type $R_1C = CR_2$, "the four groups are in one plane with the carbon, this being the plane of symmetry of all ethylene derivatives; therefore no optical activity can occur." Le Bel inclined to the view that "only so much is known about the positions of the four groups, that of the two pairs one pair lies nearer to one carbon, the other pair to the other carbon. . . . Ethylene derivatives may have no symmetry in their molecules; they may be active."

Two tetrahedral arrangements are given by van't Hoff for the atoms in a molecule $R_1R_2C = CR_1R_2$. If the figures are projected on to a plane surface they are represented by the formulæ

$$R_1CR_2 \quad \text{and} \quad R_1CR_2$$
$$\overset{\|}{R_1CR_2} \quad \overset{\|}{R_2CR_1}$$

These formulæ provide for a kind of isomerism which was unforeseen by the older conceptions that thought of the atoms as arranged in one plane. Isomerides of this type will differ in stability, because the hypothesis "assumes a difference in the analogous dimensions" of their molecules. According to van't Hoff, two isomerides can always exist of the type $(R_1R_2)C = C_{2n+1} = C(R_3R_4)$ when R_1 and R_2, as well as R_3 and R_4, are different; as the models of these isomerides are enantiomorphous, the compounds will be optically active. Compounds of the type $(R_1R_2)C = C_n = C(R_3R_4)$, where the four groups are not the same, will show isomerism but not optical activity.
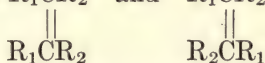
The arrangement of a molecule formed by trebly linking a pair of carbon-atoms, $R_1C \equiv CR_2$, is represented by two tetrahedra with three summits in common, and therefore a surface

of each coinciding so that they form a double three-sided pyramid; as no difference is possible in the relative positions of the univalent groups R_1 and R_2, isomerism is impossible.

It might appear at first sight that the fundamental idea of stereochemical formulæ—the molecule is a stable system of material points which may be assumed to be motionless—would lead to a less elastic representation of isomerism than that gained by using the older view which, on the whole, regarded structural formulæ as expressions of reactions, and was not seriously concerned with the spatial arrangement of the parts of molecules. The opposite of this has happened. When we think of two tetrahedra with a summit of one joined to a summit of the other, and an atom of carbon in the centre of each, we think not only of the possibility of arranging in different ways the six atoms, or groups of atoms, placed at the six unoccupied summits, but also of the possibility of rotating one or both of the tetrahedra, and thereby changing the relative positions of the atoms which are directly joined to the two atoms of carbon; we recognize the possibility of a finer kind of isomerism than any suggested by the older one-plane formulæ. The mutual actions of the six atoms, or groups (we may say, the affinities of the six radicals), will determine the position of maximum stability.

We may go a step further and suppose that some change in the external conditions—increase of temperature, or the juxtaposition of the molecules of another substance, for example— may produce so great a strain that the atomic system changes to another which is more stable under the new conditions, without completely breaking down. Of the two stable configurations, one may persist throughout a wider range of conditions than the other. We thus recognize the possibility of the existence of a more stable, and of a less stable, form of the same compound. And we see that it may be necessary, as indeed it has become necessary in some cases, to express the reactions of a compound by more than one formula. (Compare Chapter XVI.)

A rich crop of results has been gained by applying the stereochemical hypothesis in these directions. I would draw attention more particularly to a memoir by Wislicenus, pub-

lished in 1887,[1] wherein the possible configurations of various molecules are considered in detail, and the stereochemical hypothesis is applied in great fulness to many cases of isomerism. Speaking of the configuration of maximum stability of a molecule, Wislicenus says:[2]

"Heat impulses of small intensity will give rise only to swinging of the systems about the position corresponding to their most active affinities; more energetic impulses, however, may overcome this direct attraction, and as a result one system will rotate with respect to the other. In a molecular aggregate at sufficiently high temperatures, there must always exist some configurations which do not correspond to the position of greatest attraction. Their number will increase as the mean temperature of the mass rises. But the position assumed as a result of the strongest attractive force is the most *favourable* position; and even at high temperatures this favourable configuration is present in greater numbers than any other configuration which may be produced by the heat impulses. . . . If the four radicals combined with a single carbon-atom attract one another with unequal affinities, the position of the valencies of this carbon-atom must suffer some change. The model of the carbon system is then no longer a regular tetrahedron, as has been pointed out by van't Hoff. Such a deviation will also take place when a similar relation of the affinities exists between the radicals combined with two atoms of carbon . . . in that the pair of atoms with the strongest affinities will tend to approach a little nearer to each other."

In his address[3] at the *Feier zu Ehren August Kekulé*, von Baeyer spoke of the forces which determine the stability of molecules. Referring to the molecule of ethane (C_2H_6), he said: "The two atoms of carbon are pressed together by a force which corresponds with the resultant of the attractive forces of all the atoms in the direction of the line of union of the two carbon-atoms." He spoke of this force as a *pressure*. The two atoms of carbon in ethylene (C_2H_4) are said to be joined by a double bond, because either "the absence of two hydrogen-atoms lessens the strength of the attraction of carbon-atom and carbon-atom," or "the two affinities no longer act in the same

---

[1] " Ueber die räumliche Anordung der Atome in organischen Molekulen und ihre Bestimmung in geometrisch-isomeren ungesättigten Verbindung." *Abhand. der math- phys. Classe der Köntgl. Säch. Gesell. Wiss.*, **14**, 1 [1887]. An English translation of this memoir was published along with translations of the memoirs by Pasteur, Le Bel, and van't Hoff, already referred to, with the title "The Foundations of Stereochemistry," as No. XIII of *Scientific Memoirs*, by the American Book Company. [No date, probably about 1900.]

[2] The quotation is from the American translation.

[3] *Berichte*, **23**, 1265 [1890].

direction as in methane." The second of these suggestions was favoured by von Baeyer, because, in ring-compounds of several methylene (CH_2) groups, the greatest instability is found in that ring (trimethylene) wherein Kekulé's model [1] shows the greatest deviation of the axes. The weakening of the attractions is thus thought of as due to changes in the directions of the individual affinities. The affinity of atom for atom may be represented by elastic wires; von Baeyer spoke of it as a *tension*. Pressure and tension, he said, work in opposition, and may completely neutralize one another.

"Thus it is thinkable that, by a strong pressure, the double linking acquires properties which are similar to those of a single linking, and that such a pressure may be brought about by replacing atoms of hydrogen by other groups." [2]

The stereochemical hypothesis has given more definite meanings to the expressions, 'single,' 'double,' and 'treble bonds,' and has helped to disperse the confusion which so long prevailed between the conceptions of atomic equivalency and atomic affinity.[3] The hypothesis has had these clarifying effects by introducing into chemistry a more rigid and more precise mechanical picture of the molecule as an atomic structure than any which had been formed before, by describing bonds as the directions wherein the affinities of atoms act irrespectively of their strengths, and by regarding the spatial arrangement of atoms, and hence the stabilities of molecules, as conditioned not only by atomic linkings but also by atomic affinities, which together determine the greater or less proximity of the atoms to one another. This conception of molecular structure, and this view of the connexion between molecular structure and the affinities of the atoms, have been advanced by the results of the investigation of the affinity-constants of acids and bases. The main lines of these investigations will be traced in Chapter XIV.

---

[1] See p. 296.

[2] Von Baeyer has developed his "Strain" theory of benzene in a series of memoirs, the most important of which are in *Annal. Chem. Pharm.*, **245**, 103; **251**, 257; **256**, 1; **258**, 1, 145; **266**, 169; **269**, 145.

[3] An interesting chemico-geometrical development of the fundamental hypothesis of stereochemistry, especially to benzene and its derivatives, will be found in two communications by H. Sachse in *Zeitsch. für. physikal. Chemie*, **10**, 203 [1892]; and **11**, 185 [1893].

The prediction has been confirmed which was made by Kekulé in 1861, when he said [1] that a knowledge of "the constitution of material things, or . . . of the arrangement of atoms, can be attained, not by the study of chemical metamorphoses, but much more by a comparative examination of the physical properties of the persisting compounds." This part of the history of molecular structure will be dealt with, in outline, in the last chapter of this book.

The stereochemical hypothesis has been strengthened and advanced by the discovery of optically active compounds wherein an atom of nitrogen is directly linked to five different atoms and groups of atoms, and by the isolation of optically active compounds of quadrivalent sulphur, of quadrivalent tin, and of certain other quinquivalent and quadrivalent atoms.[2] A beginning has been made in the application of the hypothesis to inorganic compounds.[3]

The history of the classification of homogeneous substances shows a series of attempts to put together those substances which were found to be similar in composition and similar in reactions. It shows a gradual refining of the conceptions of composition and reactions. Unlooked for reactions were discovered, unlooked for because they were the reactions of compounds whose compositions were identical. Isomerism was recognized. But how was it possible that compounds should react differently and be composed of the same quantities of the same elements? It was necessary to make a finer analysis of the idea of composition. The results of the analysis found no expression except in the language of a theory, the theory of molecules and atoms. At a later time, identity of composition was found to be sometimes associated with differences in certain physical properties, and with identity of chemical reactions, or with differences in reactions so slight that they could

---

[1] *Lehrbuch*, I, 158.

[2] See, especially, Pope and Peachey, *C. S. Journal*, 75, 1127 [1899]; 77, 1072 [1900]: and Pope and Harvey, *C. S. Journal*, 79, 828 [1901]. Also, Archibald and McIntosh, *C. S. Journal*, 86, 919 [1904]. For a review of the knowledge of the stereochemistry of compounds of nitrogen to the year 1904, see H. O. Jones, *Brit. Ass. Reports* for 1904, pp. 1–24. See also van't Hoff's *The Arrangement of Atoms in Space*, pp. 169–183.

[3] See Appendix, by A. Werner, to *The Arrangement of Atoms in Space*.

not be expressed by the formulæ in common use. A further refinement of the idea of composition was demanded, and was made by developing the fundamental postulates of the molecular and atomic theory.

When that latest development of the atomic theory was announced, it was welcomed by some, and scorned by some chemists of light and leading. Notable among the scorners was Kolbe, a man who had a genius for criticising the work of those from whom he differed without troubling to understand it. Kolbe was indignant that a young man, a chemist 'as good as unknown,' should have dared to think about the arrangement of atoms in space, to enter a path wherein no 'true natural philosopher' had ventured to walk. The memoir of van't Hoff was denounced as 'an hallucination' and 'a silly phantasy.' Nevertheless it remained true that 'babes' sometimes see what is hidden from the 'wise and prudent.'

CHAPTER XII.

APPLICATIONS OF THE HYPOTHESIS OF IONIZATION TO THE CLASSIFICATION OF HOMOGENEOUS SUBSTANCES.

I BEGIN this chapter by again reminding the student that I am not attempting to do more than to trace the main lines of advance of the principles of chemistry. I am not writing a history of chemistry. Much less am I trying to write a history of chemical physics, or of physical chemistry.

Lavoisier and his followers thought of an acid as the union of a simple or a compound acidifiable base with the acidifying principle, and, for them, the acidifying principle was oxygen. About sixty years after Lavoisier's time, Liebig, following Davy, declared acids to be compounds of replaceable hydrogen with certain radicals, and salts to be compounds of metal with the same radicals. The main lines of advancement of these conceptions have been traced in pp. 226–232 of Chapter VIII.

In the twenties of the nineteenth century, Berzelius promulgated his doctrine of electrodualism. To make the facts concerning the electrical properties of substances directly applicable to chemical classification, he adopted the hypothesis that the electricity of every radical, of every element, and therefore of every atom, is concentrated in two opposite poles, one of which is stronger than the other, and therefore, each radical, element, atom, has a specific unipolarity which determines its general chemical character; and that the more intense is the polarity of an atom, element, radical, the greater is its affinity, because "affinity is the action of the electric polarities of particles." This hypothesis led Berzelius to assert that any chemical reaction strives towards the establishment of electrical neutrality, but no compound is absolutely neutral; that every

compound is a dual structure of an electrically positive and an electrically negative simple or compound radical; and that the formation of a product chemically like the parent-substance can happen only when the positive part thereof is replaced by an element, or by a radical which is positive towards the negative part of the original substance, or, the negative part, by an element or by a radical which is negative relatively to the positive part of the parent-substance.

The main lines of development of Berzelian dualism have been traced in pp. 244–249 of Chapter IX.

Between 1885 and 1890, chemists were taught by van't Hoff, and by Arrhenius, to realize that those dilute solutions of homogeneous substances which exert equal osmotic pressures at the same temperature, contain equal numbers of molecules of the dissolved substances; and to use the supposition that in dilute aqueous solutions of most acids, bases, and salts, the molecules, or some of the molecules of those compounds are separated into particles which carry electric charges: chemists were taught to recognize vividly the chemical importance of the conception of ions. Some of the chief lines of development of the notion of ionization have been traced in Chapter V.

We must now more fully open the history of the applications of the hypothesis of ionization to the classification of homogeneous substances.

In Chapter VIII, page 232, I mentioned that Daniell (between 1839 and 1844) represented the effect of the current on aqueous solutions of many salts to be the separation of each salt into two parts, a cation which is the metal of the salt, and an anion which is what Liebig had called the radical of the salt; and (Chapter VIII, p. 238) that he pictured the electrolysis of salts of ammonia as the separation of them into the cation ammonium (NH_4), and anions or negative radicals. I also noted the fact that Hittorf (1853 to 1859) extended the work begun by Daniell, and expressed his results in the general statement—acids, bases, and salts are electrolytes.

Before giving an account of Daniell's work, I must refer to a generalization of fundamental importance established by Faraday in 1834.

In his *Experimental Researches in Electricity*, Faraday established the *law of constant electrochemical action:* [1]

"*The chemical power of a current of electricity is in direct proportion to the absolute quantity of electricity which passes.*"

Faraday measured 'the chemical power of a current,' or the amount of chemical action done by a current, by the quantities of the ions liberated during electrolysis. Defining 'electrochemical equivalents' as "the numbers representing the proportions in which *ions* are evolved," and taking as unity the quantity of electricity which evolves one gram of hydrogen, he showed that the quantities of different ions which are evolved by this quantity of electricity, that is, their electrochemical equivalents, are the same as the ordinary chemical equivalents.

"The equivalent weights of bodies are simply those quantities of them which contain equal quantities of electricity, or have naturally equal electric powers; it being the ELECTRICITY which *determines* the equivalent number, *because* it determines the combining force. Or, if we adopt the atomic theory or phraseology, then the atoms of bodies which are equivalent to each other in their ordinary chemical action, have equal quantities of electricity naturally associated with them." [2]

In his memoir of 1834, Faraday defines the terms which he introduced for the purpose of expressing the phenomena of *electrolysis*.[3]

"Many bodies are decomposed directly by the electric current; their elements being set free; these I propose to call *electrolytes* (ἤλεκτρον, and λύω, *solvo*). . . . Then for *electrochemically decomposed* I shall often use the term *electrolyzed*." . . . "In place of the term pole, I propose using that of *Electrode* (ἤλεκτρον, and ὁδὸς, *a way*), and I mean thereby that substance, or rather surface, whether of air, water, metal, or any other body, which bounds the extent of the decomposing matter in the direction of the electric current." . . . "If the magnetism of the earth is due to electric currents passing round it, the latter must be in a constant direction, which, according to present usage of speech, would be from east to west, or, which will strengthen this help to the memory, that in which the sun appears to move. If in any case of electrodecomposition we consider the decomposing body as placed so that the current passing through it shall be in the same direction, and parallel to that supposed to exist in the earth, then the surfaces at which

[1] *Experimental Researches in Electricity*, vol. i, series vii, p. 231. Vol. i of the *Researches* contains fourteen memoirs communicated to the Royal Society from 1831 to 1838.
[2] Series vii, p. 256.
[3] *Researches*, series vii, pp. 197, 198.

the electricity is passing into and out of the substance would have an invariable reference, and exhibit constantly the same relations of powers. Upon this notion we purpose calling that towards the east the anode ($\H{\alpha}\nu\omega$, up-*wards*, and $\hat{o}\delta\acute{o}\varsigma$, *a way*, the way which the sun rises), and that towards the west the *cathode* ($\kappa\alpha\tau\grave{\alpha}$, *downwards*, and $\hat{o}\delta\grave{o}\varsigma$, *a way*, the way which the sun sets)." . . . "Finally, I require a term to express those bodies which can pass to the *electrodes*. . . . I propose to distinguish such bodies by calling those *anions* ($\grave{\alpha}\nu\iota\grave{\omega}\nu$, *that which goes up* [neuter participle]) which go to the *anode* of the decomposing body; and those passing to the *cathode*, *cations* ($\kappa\alpha\tau\iota\grave{\omega}\nu$, *that which goes down*); and when I have occasion to speak of these together, I shall call them *ions*."

Daniell started from the fundamental principle that "the force which is measured by its definite action at any one point of a circuit cannot perform more than an equivalent proportion of work at any other point of the same circuit." Applying this principle to the results of the measurements he made of the quantities of hydrogen and oxygen severally liberated at the cathode and anode during the electrolyses of aqueous solutions of sulphuric acid, sodium sulphate, and potassium sulphate, and of the quantities of the same gases liberated by passing the same current, simultaneously, through acidulated water, Daniell[1] concluded that the water was not decomposed in the changes, but only the acid or the salt was electrolyzed. In the case of sodium sulphate, for example, he concluded that the salt was separated into two ions, "an anion composed of one equivalent of sulphur and four equivalents of oxygen, and the metallic cathion sodium"; and that secondary reactions then occurred between the anion and water whereby sulphuric acid (SO_3) and oxygen were formed, and between the cation and water whereby soda and hydrogen were produced. Daniell gave the following *electrolytic formulæ*, as he called them, to the salts he examined, and compared these with the *chemical formulæ* which were then used for these salts.

	Chemical Formula.	Electrolytic Formula.
Sulphate of soda.	$(S+3O)+(Na+O)$	$(S+4O)+Na$
Sulphate of potassa. . . .	$(S+3O)+(P+O)$	$(S+4O)+P$
Nitrate of potassa.	$(N+5O)+(P+O)$	$(N+6O)+P$
Phosphate of soda.	$(P+2\frac{1}{2}O)+(Na+O)$	$(P+3\frac{1}{2}O)+Na$
Sulphate of copper.	$(S+3O)+(Cu+O)$	$(S+4O)+Cu.$

Similar reasoning applied to the results of his measurements of the quantities of hydrogen given off, ammonia formed, and metal of the cathode dissolved, during the electrolyses of aqueous solutions of salts of ammonia, led Daniell to the conclusion that these salts are compounds of negative ions with the positive radical ammonium. "Muriate of ammonia," he said, "proved to be an electrolyte whose simple *anion* was chlorine, and compound *cathion* nitrogen with four equivalents of hydrogen Its electrolytic symbol, therefore, instead of being $(C^h + H) + (N3H)$ would be $C^h + (N + 4H)$."

Daniell noted the agreement between his results and Davy's view of the constitution of acids and of salts—"a radical forms an acid with hydrogen, and a salt with sodium or any other metal." He also drew attention to the support which his results gave to the ammonium hypothesis of Berzelius.

In 1840, Daniell [1] proposed to use the names "oxysulphion of hydrogen," "oxysulphion of copper," "oxynitrion of potassium," and other names formed similarly to these, when he was speaking of the phenomena shown in the electrolyses of sulphuric acid, sulphate of copper, nitrate of potassium, and other acids and salts.

In a memoir published in 1844, Daniell and Miller [2] described quantitative experiments on the electrolyses of solutions of various complex salts, such as double sulphates, the three phosphates of sodium, and ferrocyanide and ferricyanide of potassium. They described electrolytes as compounds of equivalent quantities of two, or more than two ions each of which is sometimes an element and sometimes a group of elements.

The conception of the electrolysis of a compound which prevailed in the forties of last century was described by Daniell and Miller as "definite decomposition with equivalent and opposite transfer of the elements or radicals of the compound to the opposite electrodes of the battery." According to this view, the concentrations of the liquids around the cathode and the anode must decrease equally, because equivalent quantities of the two ions must be transferred to the electrodes. The results

---

[1] *Phil. Trans.* for 1840, p. 209. For a systematic nomenclature of ions, see Walker, *Chem. News*, 84, 162 [1901].
[2] *Phil. Trans.* for 1844, p. 1.

of the measurements made by Daniell and Miller showed that, although the quantities of the anion and the cation liberated at the electrodes are always strictly equivalent, nevertheless the number of cations which travel to the cathode, in a determinate time, is not so large, in many cases not nearly so large, as the number of anions which travel to the anode in the same time.

Daniell and Miller were unable to devise a means for studying in detail the rate of transfer of ions to the electrodes. This problem was solved by Hittorf [1] in the years 1853 to 1859. He showed by a simple mechanical analogy that equivalent quantities of cations and anions may be liberated at the electrodes although the rates of motion of the ions are not the same. Let there be six compound particles of an electrolyte on each side of a porous diaphragm; let C be the cathode and A the anode. We have the arrangement represented in I, where the concentration of the electrolyte around the cathode is equal to that

I.

```
C                    A
 | + + +  :  + + + |
 |        :        |
 | - - -  :  - - - |
```
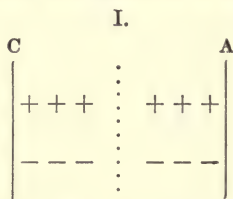
around the anode, and each is expressed by the number 3. When the current passes, suppose that only the cations move; when three cations are discharged and liberated, three anions also are discharged and liberated. There are now three compound particles around the cathode, and none around the anode; the concentration around the cathode is 3, that around the anode is nil. The state of affairs is represented in II.
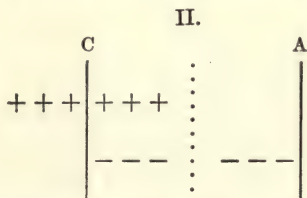
II.

```
       C                A
+ + + | + + +  :        |
       |       :        |
       | - - - :  - - - |
```

Suppose that the cations and the anions move equally rapidly: when one cation has left the anodic space, one anion has left the space around the cathode, and two ions of each kind are discharged and liberated; the concentration has been reduced in each compartment from 3 to 2. Diagram III represents the condition of affairs.

III.
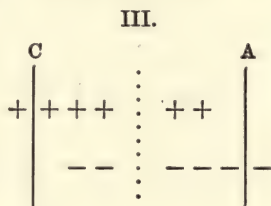
Now suppose that the cations move twice as quickly as the anions. When three cations and three anions are discharged and liberated, we have the distribution shown in IV, where the concentration around the cathode has been reduced from 3 to 2, and that around the anode from 3 to 1.

IV.
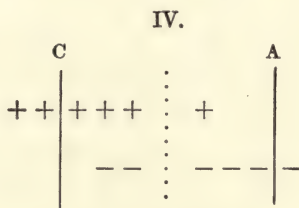
The decrease of concentration around either electrode is evidently proportional to the rate of movement of the ions leaving that space. Hence,

$$\frac{\text{decrease of concentration around the anode}}{\text{decrease of concentration around the cathode}} = \frac{\text{speed of cations}}{\text{speed of anions}}.$$

The moving ions transport the electricity: as each ion bears the same quantity of electricity, the share of each in the transport is proportional to its rate of motion. If u and v are the several rates of movement of the cation and the anion, then $\frac{u}{u+v}$ represents the cation's share, and $\frac{v}{u+v}$ represents the anion's share in the transport of the electricity.

The values of these expressions are Hittorf's *transport-numbers (Ueberführungszahlen)*.

Hittorf determined the transport-numbers for the ions of many salts by measuring the concentrations around the electrodes at the beginning of an experiment, and after a feeble current had passed for some time. He describes in detail the apparatus which he used.

Hittorf advanced step by step, establishing each step by careful experiments, until he arrived at a clear conception, which has borne much chemical fruit, of the conduction of electricity in electrolytes, and of the part played by the electrolytes. The wide range of applicability of Hittorf's experimental methods, and the suggestiveness of his views, were not realized until more than thirty years after the publication of his memoirs.

In a memoir published in 1857, Clausius [1] reasoned somewhat as follows. If the ions of an electrolyte are bound together into complete molecules in a solution of the electrolyte, a certain amount of electrical energy must be used in tearing the ions apart. Therefore a current will not pass through a solution of an electrolyte until the electromotive force is sufficient to overcome the mutual attractions of the ions; but, as soon as the necessary electromotive force is attained, a large number of molecules must be decomposed at the same time, because "all the molecules are under the influence of the same force and their relative positions are alike." Clausius stated his conclusion thus: "So long as the active driving force is less than a certain limiting value, no current will pass; but when the force exceeds this limit, a very strong current will suddenly be produced." This conclusion is entirely opposed to the facts. The facts established by Faraday show that the smallest electromotive force produces a current, and that the intensity of the current increases in proportion to the force; in other words, that Ohm's law —the quantity of electricity which passes in unit time is directly proportional to electromotive force, and inversely proportional to the resistance of the conductor—holds good for all values of the electromotive force. Clausius arrived at the conclusion that "the semi-molecules [ions] of an electrolyte cannot be

[1] *Pogg. Annal.*, **101**, 338 [1857].

firmly held together so as to form complete molecules which are disposed in a definite and regular manner."

Hittorf adopted this conclusion, and pictured the solution of an electrolyte as containing particles which are constantly exchanging their ions. He identified the processes which happen between two electrolytes in contact with the chemical changes which occur between the same compounds. Hittorf said:

"All compound substances which are good conductors of electricity always exchange their ions when they are brought into contact in the liquid state." . . . "Electricity can evoke this exchange only between the molecules of those compounds which manifest a like exchange when they react, in the ordinary phenomena of affinity, with other substances constituted similarly to themselves." . . . "All electrolytes are salts, in the meaning given to that word by the newer chemistry.[1] The exchange which happens during electrolysis, and that which occurs by the action of double affinity, is an exchange between the same constituents of the molecules of salts. This exchange is the means of that transmission of molecular motion which we call the electric current."

In these sentences, and in the facts which these sentences summarize, Hittorf laid the foundations of that part of the theory of electrochemical action which asserts that the readiness wherewith electricity is transported by the ions of an electrolyte s proportional to the rapidity of the chemical reactions which are dependent on that electrolyte. The difficulties which Hittorf found in applying his conceptions to some classes of facts were removed, about thirty years later, by Arrhenius, who boldly asserted that solutions of electrolytes must actually contain many free ions.

Hittorf not only traced the close analogy between the chemical reactions, and the electrical conductivities of solutions of electrolytes, that is, of salts,[1] he also clearly distinguished between the rates of conductivity of electrolytes and the strengths of the affinities between their ions. He showed that many electrolytes whose parts were supposed to be held together by strong affinities conduct electricity, when in solution, much more rapidly than others between the parts of which there was

---

[1] For an account of the development of Hittorf's dictum, "*All Electrolytes are Salts*," see Chapter XVI.

supposed to be only weak affinities. As his measurements of the migrations of ions showed that electricity is carried by the parts of molecules, it followed that the strong affinity which was supposed to hold together the parts of the molecule of potassium chloride, for example, is overcome when that salt is dissolved in water. "We must distinguish," Hittorf said, "between the decomposability of a compound by the current and that which is based on ordinary chemical means." Again, he said: "Nothing is less warranted than the assumption of a proportionality between the electric resistance of a compound and the affinities which the prevailing chemical views ascribe to its ions."

Finally, I ask the student to notice that Hittorf was much impressed by the similarities between the conditions of substances in solution and in the state of gas. "The analogies," he said, "between substances in solution and gaseous substances force themselves on the attention of every one who is concerned with the exact study of the phenomena of solutions."

These analogies were developed by van't Hoff in 1887, and made the basis of a very fruitful generalization, which states that "equal volumes of the most different solutions, measured at the same temperature and the same osmotic pressure, contain an equal number of molecules, and that is the number which is contained in an equal volume of a gas at the same temperature and pressure."

In Chapter V we saw that this generalization was the outcome of the application of thermodynamical reasoning to the facts (many of which were established by the experimental researches of Raoult) concerning the connexions between the osmotic pressures of dilute solutions and the depressions of the freezing-points, and of the vapour-pressures of the solvents caused by dissolving in them the different homogeneous substances used to make the solutions. Furthermore, we saw, in the same chapter, that van't Hoff explained the apparent deviations from his law by following the analogy of gases, and supposing that in dilute aqueous solutions many salts, that is, many electrolytes, are separated, more or less completely, into their ions which move independently of one another.

We are told by van't Hoff that he would not have ventured

to propound an Avogadrean law for solutions "had not Arrhenius convinced me, in a letter, that in the cases of salts and similar compounds we have probably to do with separations into ions." Solutions which do not apparently follow the van't Hoff-Avogadro generalization conduct the electric current; and the deviations which they show from the law, van't Hoff said, "can be calculated from their conductivities by using the assumption which has been made by Arrhenius."

In Chapter V (pp. 166, 167) I wrote as follows:

"The whole subject of the condition of those homogeneous substances which conduct electricity in aqueous solutions was investigated by Arrhenius in memoirs of extreme importance. He supposed that a certain fraction of the molecules of a dissolved electrolyte is separated into ions in a dilute solution, and the ions move independently of one another; such molecules he called *active*, and he applied the term *inactive* to the other molecules whose ions were supposed by his hypothesis to be firmly bound together. Arrhenius calculated values for van't Hoff's factor i, on the hypothesis that i expressed the ratio between the actual osmotic pressure of a substance in solution and the osmotic pressure which it would exert if it consisted only of inactive molecules.[1] On this basis, Arrhenius developed an electrolytic theory of chemical reactions between substances in solution."

The electrolytic theory of Arrhenius will not be described until I am dealing with the history of chemical affinity (in Chapter XIV); it is necessary, however, to say a few words about it here.[2]

Arrhenius referred the conductivities of electrolytes to equal weights of them in solution. His measurements showed that conductivity increases as dilution with water increases, until a maximum limiting value is attained which is approximately the same for each class of compounds—acids, bases, and salts. He supposed that only some of the molecules of an electrolyte take part in transporting the electricity, only some of the molecules are *active*, that is, ionized; and that dilution increases the ratio of active to inactive molecules. He showed that the chemical reactivity of an electrolyte, as well as its electrical conductivity, is dependent on the ratio of ionized to non-ionized molecules; and he established a method for calculating this ratio from ob-

---

[1] This factor was introduced by van't Hoff to enable him to bring Guldberg and Waage's law of mass-action into keeping with observations of osmotic pressure; he said that the factor depended on the molecular concentrations of the solutions. (See Chapter V, p. 166.)

[2] Arrhenius, *Zeitsch. für physikal. Chemie*, **1**, 631 [1887].

servations of conductivity at different concentrations. By connecting van't Hoff's factor i (see p. 166) with the conductivities of solutions of electrolytes, Arrhenius established an immediate interdependence of the electrical conductivities and the depressions of the freezing-points, and, hence, of the osmotic pressures of these solutions.

Clausius had thought of electrolytic conductivity as dependent on molecular instability, as conditioned by the readiness wherewith the molecules of the electrolyte exchange their ions. Arrhenius went a step further, and declared that we must think of the ions as moving in complete independence of one another. The Clausian hypothesis indicated that conductivity would decrease as dilution increased; because, if there is only a very small number of molecules of an electrolyte moving among a very large number of molecules of water—say, one molecule of electrolyte to 50,000 molecules of water—the chances of ionic interchange are smaller than when the relative number of electrolizable molecules is large. But it is just at such dilutions as 1 to 50,000 molecules that the maximum conductivity of an electrolyte is reached.[1]

By connecting the chemical reactivities of electrolytes with the movements of their free ions, Arrhenius taught chemists to think of the reactions of electrolytes in dilute solutions as the reactions of the ions of these compounds, and to distinguish the reactions of electrolytes from those of compounds, especially many classes of compounds of carbon, which do not conduct the electric current.

The hypothesis that the reactions of electrolytes—that is, of acids, bases, and salts [2]—are the reactions of the ions of these compounds, has produced a great clarifying effect on the study of the chemical changes which are made use of in qualitative and quantitative analyses. This branch of the theory of electrochemical reactions was developed by Ostwald in his book, *Die Wissenschaftlichen Grundlagen der Analytischen Chemie*, published in 1894.[3]

---

[1] Compare Ostwald, *Lehrbuch der Allgemeinen Chemie*, ii, 549,–550.
[2] See foot-note on p. 329.
[3] An English translation, entitled *The Scientific Foundations of Analytical Chemistry*, appeared in 1895.

The theory of Arrhenius also differentiated the reactions of certain compounds when dry from those of aqueous solutions of the same compounds, and distinguished the reactions of aqueous solutions of some compounds from those of solutions of the same compounds in solvents other than water. For instance, dry liquid hydrogen chloride (HCl) is a non-conductor and does not react with carbonates; a solution of this compound in dry chloroform scarcely reacts with carbonates, and has an exceedingly small electric conductivity; an aqueous solution of hydrogen chloride conducts electricity rapidly and reacts as a strong acid. (For an account of later developments of the view that chemical reactivity is always accompanied by ionization, see Chapter XVI.) The theory of Arrhenius has opened wide fields of research to be cultivated both by the chemist and the physicist, and has been instrumental in founding and developing the new science of physical chemistry.

The theory of the ionization, or electrolytic dissociation of salts, pictures an aqueous solution of an acid—a salt of hydrogen —as containing many free ions of hydrogen, each carrying one positive electric charge, and many free ions of acidic radical, each carrying such a number of negative charges that the total number of positive charges on the cations of hydrogen is equal to the total number of negative charges on the anions or radicals; it pictures an aqueous solution of a metallic salt as containing many metallic cations and an equivalent number, equivalent chemically and electrically, of anions which are acidic radicals; and it bids us think of an aqueous solution of a base—a metallic hydroxide—as containing equivalent numbers of metallic cations and hydroxylic anions. The theory of ionization has confirmed, extended, and intensified that view of the constitution of acids and salts which was adumbrated by Dulong, used hesitatingly by Davy, and firmly established on a chemical basis by Liebig.

The *Faraday Lecture* delivered by Helmholtz in 1881, did much to clarify the ideas of chemists concerning the bearing of Faraday's work on electrochemical phenomena.[1] If the ex-

---

[1] "On the Modern Development of Farady's Conception of Electricity," *C. S. Journal*, **39**, 277 [1881].

istence is accepted of freely moving ions in the solution of an electrolyte when a current is passing, then, according to Helmholtz, Faraday's law tells us that,

"The same definite quantity of either positive or negative electricity moves always with each univalent atom, or with every unit of affinity of a multivalent atom, and accompanies it during all its motions through the interior of the electrolytic fluid. This quantity we may call the electric charge of the atom."

In another passage Helmholtz expresses Faraday's law in these words:

"The same quantity of electricity passing through an electrolyte either sets free, or transfers to other combinations, always the same number of units of affinity at both electrodes. . . ."

Helmholtz's reading of the law of Faraday teaches us to think of a univalent atom as an atom which carries unit electric charge, of a bivalent atom as one which carries two unit charges, of an n-valent atom as one which carries n unit charges. We thus get a physical basis for the chemical notion of valency, and we are enabled to attach a more definite meaning than formerly to the expressions, 'single,' 'double,' 'treble bonds,' or 'linkings of atoms.' I shall return to this part of the subject immediately, when considering the more recent development of the meaning of the expressions, 'positively charged' and 'negatively charged' particles.

In the quotations I have given from his *Faraday Lecture*, Helmholtz speaks of a quantity of electricity as moving with every *unit of affinity* of a multivalent atom, as setting free or transferring the same number of *units of affinity*. We must interpret a *unit of affinity* to mean *a simple atomic linking*, or *a valency;* it does not mean a unit of chemical affinity. Helmholtz shows that Faraday's work disproved the Berzelian notion that the chemical affinity of an atom can be measured by the quantity of electricity on the atom.

"A fundamental point which Faraday's experiment contradicted was the supposition that the quantity of electricity collected on each atom was dependent on their mutual electrochemical differences, which Berzelius considered as the cause of their apparently greater chemical affinity."

In another part of his *Lecture*, Helmholtz says:

"According to Berzelius' theoretical views, the quantity of electricity collected at the point of union of two atoms ought to increase with the strength of their affinity. Faraday demonstrated by experiment that so far as this electricity came forth in eletrolytic decomposition, its quantity did not at all depend on the degree of affinity. This was really a fatal blow to the Berzelius' theory."

Some compounds readily take part in many chemical reactions which proceed rapidly; others do not interact so readily nor so rapidly at ordinary temperatures. Chemists had long been accustomed to think of the constituents of the first class of compounds as held together by strong affinities; but, speaking broadly, it is these compounds which are the best electrolytic conductors when in solution, that is, it is these compounds which are very readily ionized. Therefore chemical affinity cannot be measured by the quantities of electricity on atoms if the conception of affinity which prevailed at the time of Berzelius, and for many years after that time, is accepted as correct.

The foundation of Berzelian dualism was the assertion of a close connexion between electrical and chemical forces; the arguments in favour of that connexion have been greatly strengthened by the study of electrolysis. The further assertion, that a greater quantity of electricity must be required to separate a compound of a very positive and a very negative element than is needed to decompose a compound of a less positive with a less negative element, was disproved by the results of Faraday's experiments. All that has been done in the study of electrochemical changes has served to emphasize the difference between the two conceptions, atomic linking and atomic affinity.

In framing his electrodualistic theory, Berzelius confused— perhaps it was impossible at that time not to confuse—two quantities; quantity of electricity and quantity of electrical energy. Although Faraday's law was not announced until more than ten years after the promulgation of the doctrine of electrodualism, we may say that Berzelius would have regarded as nearly synonymous the two statements that equal quantities of electricity liberate masses of simple or compound radicals which are chemically equivalent, and that equal quantities of electric energy liberate equivalent masses of radicals. Unfortunately,

in ordinary usage, the word *electricity* sometimes means quantity of electricity, and sometimes electric energy. Electric energy is defined by two factors; quantity of electricity, and intensity, or pressure of electricity. The second factor is generally called potential-difference, or electromotive force. When two metals are brought into contact, an electric pressure, an electromotive force, is produced; the electromotive force produced by the contact of zinc and copper, for example, is greater than that produced by the contact of zinc and iron. From comparisons of the electric tensions of pairs of metals, Volta,[1] in 1802, arranged several metals in an electromotive series, beginning with the most electropositive. It was found that, when a more electropositive metal is immersed in a solution of a salt of a less electropositive metal, the former dissolves, and the latter metal is deposited. As the dissolution of a metal in a solution of a salt of another metal was supposed to proceed in two stages, the first of which was thought to be combination of the dissolving metal with oxygen, Berzelius regarded the arrangement of metals in the electromotive series as an arrangement in terms of their affinity for oxygen; and he concluded that a close connexion exists between the positions of metals in the series—that is, between their greater or less positivity—and their chemical affinities. Berzelius extended the notion of electrical positivity and negativity to all the elements. (Compare Chapter IX, pp. 245–246.)

Looking back, we see that Davy had a more accurate conception than Berzelius of the connexion between chemical affinity and electrical energy, for, in 1807, Davy said: "This principle [degree of electrical energy determines combination] would afford an expression of the causes of elective affinity, and the decompositions produced in consequence."[2]

The terms electropositive and electronegative have been retained by chemists as useful labels for two classes of elements which show certain broadly marked differences of chemical behaviour. (Compare Chapter VIII, pp. 238–239.) We do not now consider a very positive element to be one whose atoms

carry a large positive charge of electricity; we rather think of it as an element which is readily ionized, an element which has a great *tendency* towards ionization. Ostwald speaks of it as an element which has a great *affinity for electricity*.[1]

"The word *tendency*," Ostwald says,[2] "expresses a difference in the intensity of a quantity of energy; and, as we are dealing with two states of a substance which are chemically different, the *tendency* is a difference of intensity of chemical energy. A mechanical relation between chemical and electrical energy is given by the circumstance that the process in this case is necessarily connected with the production or the destruction of a quantity of electricity, whilst the two capacity-magnitudes are mutually proportional in accordance with Faraday's law."

In his *Faraday Lecture* Helmholtz said:

"The most startling result of Faraday's law is perhaps this. If we accept the hypothesis that the elementary subtances are composed of atoms, we cannot avoid concluding that electricity also, positive as well as negative, is divided into definite elementary portions, which behave like atoms of electricity."

The idea of the atomic structure of electricity is now being developed, especially by J. J. Thomson and his pupils. As the idea promises to have very many chemical applications, and has already borne directly on both of the fundamental questions of chemistry, it is necessary to say something regarding its progress.

"The bearing of the recent advances made in electrical science on our views of the constitution of matter and the nature of electricity" are discussed in Professor J. J. Thomson's *Silliman Lectures*, delivered at Yale University in May, 1903, and published in 1904.[3] Starting from Faraday's conception of lines of force in a magnetic field, extending it to the electric field, making the lines of force amenable to measurement by introducing the modified notion of tubes of force, or Faraday tubes, and regarding "each unit of positive electricity in the field as the origin and each unit of negative electricity as the termination of a Faraday tube," Thomson has formed a picture of the state of an electric field which has led him, aided by the

---

[1] *Lehrbuch der Allgemeinen Chemie*, ii, 873.
[2] *Lehrbuch*, ii, 789.
[3] *Electricity and Matter.* [Constable, 1904.]

results obtained in the laboratory, to conclusions of extra-ordinary importance and suggestiveness.

The phenomena of the electrolysis of liquids show that "the charges carried by the ions . . . are always an integral multiple of the charge carried by the hydrogen atom." Hence, as Helmholtz said, "we cannot avoid the conclusion that electricity . . . is divided into definite elementary portions which behave like atoms of electricity." Thomson finds strong evidence in favour of the atomic character of electricity in the facts concerning electrical conduction through gases: "Whether we study the conduction of electricity through liquids or through gases, we are led to the conception of a natural unit or atom of electricity of which all charges are integral multiples." [1]

By measuring the effects of a constant magnetic force on the motion of the particles of a gas at a very low pressure, and determining the electric force required to counteract the effect of the magnetic force, Thomson found the ratio of charge to mass for negatively electrified particles in gases at low temperatures.

"These experiments have led to the very remarkable result that the value of $\frac{e}{m}$ is the same [e = charge, m = mass of a particle] whatever the nature of the gas in which the particle may be found, or whatever the nature of the metal from which it may be supposed to have proceeded. In fact, in every case in which the value of $\frac{e}{m}$ has been determined for negatively electrified particles moving with velocities considerably less than the velocity of light, it has been found to have the constant value about 10^7, the units being the centimetre, gram, and second, and the charge being measured in electromagnetic units. As the value of $\frac{e}{m}$ for the hydrogen ion in the electrolysis of liquids is only 10^4, and as we have seen the charge on the gaseous ion is equal to that on the hydrogen ion in ordinary electrolysis, we see that the mass of a carrier of the negative charge must be only about one-thousandth part of the mass of a hydrogen atom. . . . I have proposed the name corpuscle for these units of negative electricity. These corpuscles are the same however the electrification may have arisen or wherever they may be found. Negative electricity in a gas at a low pressure has thus a structure analogous to that of a gas, the corpuscles taking the place of the molecules. The 'negative electric fluid,' to use the old notation, resembles a gaseous fluid with a corpuscular instead of a molecular structure."

---

[1] Compare Faraday's statement, quoted on p. 323: "The atoms of bodies which are equivalent to each other in their ordinary chemical action, have equal quantities of electricity naturally associated with them."

The application of similar methods to measurements of the ratio of charge to mass for the positive charge has shown that this ratio

"varies with the nature of the electrodes and with the gas in the discharge tube, just as it would if the carriers of the positive charge were the atoms of the elements which happened to be present when the positive electrification was produced. These results lead us to a view of electrification which has a striking resemblance to that of Franklin's 'one-fluid theory of electricity.' Instead of taking, as Franklin did, the electric fluid to be positive electricity, we take it to be negative. The 'electric fluid' of Franklin corresponds to an assemblage of corpuscles, negative electrification being a collection of these corpuscles. The transference of electrification from one place to another is effected by the motion of corpuscles from the place where is a gain of positive electrification to the place where there is a gain of negative. A positively electrified body is one that has lost some of its corpuscles."

As the corpuscles which are produced from very different substances are "similar in all respects," and the mass of one of them is much less than that of any known atom, "we see that the corpuscle must be a constituent of the atom of many different substances; that in fact the atoms of those substances have something in common."

Thomson then develops the notion of the atom as "an aggregation of a number of simpler systems," the corpuscle being a constituent of the simplest, or primordial system. As the corpuscle carries a charge of negative electricity, it must be "associated with an equal charge of positive electricity."

"Let us then take as our primordial system an electrical doublet with a negative corpuscle at one end and an equal positive charge at the other, the two ends being connected by lines of electric force which we suppose to have a material existence."

It may be asked, Where does *mass* come in here? The answer is, in Thomson's words: "The *whole* mass of any body is just the mass of ether surrounding [it] which is carried along by the Faraday tubes associated with the atoms of the body."

Thomson then considers the ways in which collections of "electrical doublets," supposed to be in motion, may lose kinetic energy, until the kinetic energy of the corpuscles in the atom, called by Thomson the *corpuscular temperature* of the atom, falls to the value at which aggregation into groups begins. He

pictures the formation of the chemical elements as the formation of more and more complicated groups of primordial systems.

"Thus, if we regard the systems containing different numbers of units as corresponding to the different chemical elements, then as the universe gets older, elements of higher and higher atomic weight may be expected to appear. Their appearance, however, will not involve the annihilation of the elements of lower atomic weight. The number of the atoms of the latter will, of course, diminish, since the heavier elements are by hypothesis built up of material furnished by the lighter. The whole of the atoms would not, however, all be used up at once, and thus we may have a very large number of elements existing at one and the same time. If, however, there is a continual fall in the corpuscular temperature of the atoms through radiation, the lighter elements will disappear in time, and unless there is disintegration of the heavier atoms, the atomic weight of the lightest element surviving will continually increase. On this view, since hydrogen is the lightest known element, and the atom of hydrogen contains about a thousand corpuscles, all aggregations of less than a thousand units have entered into combination and are no longer free."

It has long been a favourite speculation of chemists to think of the elements as aggregations of one substance. Davy, for example, rarely uses the term *element* in his *Elements of Chemical Philosophy* (published in 1812), but speaks of *undecompounded substances*. He slightly developes the speculation that all these substances are compounds of hydrogen "with another principle as yet unknown in the separate form," and supposes that perhaps "the same ponderable matter in different electrical states, or in different arrangements, may constitute substances chemically different."

Greater definiteness was given to the speculation that hydrogen may be the common basis of the elements, by the publication, in 1815, of two articles by Prout.[1] In his first article, Prout gave data which, he said, proved the specific gravities of thirteen elements and of about twenty compounds, in the state of gas, to be whole multiples of the specific gravity of hydrogen taken as unity. Prout took the weight of one volume of hydrogen to be the atomic weight of that element, and concluded that the

[1] Prout's articles appeared in Thomson's *Annals of Philosophy* for November, 1815, and February, 1816, vol. vi. p. 321, and vol. vii, p. 111. The first article is entitled, "On the Relation between the Specific Gravities of Bodies in their Gaseous State and the Weights of their Atoms." The second article is headed, "Correction of a Mistake in the Essay on the Relation. . . ." The articles appeared anonymously.

specific gravities of gaseous elements and compounds express their atomic weights referred to hydrogen. Hence he inferred that the atomic weights of many elements are whole multiples of the atomic weight of hydrogen. In his second article he said: "If the views we have ventured to advance be correct, we may almost consider the $\pi\rho\acute{\omega}\tau\eta$ $\H{v}\lambda\eta$ of the ancients to be realized in hydrogen; an opinion, by-the-by, not altogether new." Prout's data were very erroneous; most of the specific gravities he gives were calculated by multiplying "half the specific gravity of oxygen by the weight of the atom of the substance with respect to oxygen." He brought forward no accurately determined facts to support his conclusions.

In a memoir published in 1859, Dumas considered the question of the relations between the values of atomic weights from the position of the careful and accurate experimentalist.[1] He concluded that the atomic weights of many elements are whole multiples of that of hydrogen taken as unity, and those of many other elements are whole multiples of that of hydrogen if the latter is taken as ·5; that the relations between the atomic weights of many elements which exhibit analogous properties may be expressed by such simple ratios as 1:1 and 1:2; that in some groups of three similar elements, the atomic weight of the intermediate element is equal to the mean of the atomic weights of the two extremes; and that, considering those atomic weights which had then been accurately determined, "three distinct categories are found wherein the equivalents [atomic weights] appear to be multiples of 1, of ·5, or of ·25 by a whole number." In another part of the same memoir Dumas says: "All the equivalents [atomic weights] of the simple bodies or the radicals of mineral chemistry appear to be multiples of a certain unity which should be equal to ·5 or ·25 of the weight of the equivalent of hydrogen."

The results of Stas extraordinarily careful determinations of atomic weights [2] finally disproved the supposition that the atomic weights of a large number of elements are whole multiples of that of hydrogen taken as 1, as ·5, or as ·25.

---

[1] "Mémoire sur les équivalents des corps simples," *Annal. Chim. Phys.*, [3] **55**, 129 [1859].

[2] For references to Stas' memoirs, see footnote, p. 94, Chapter III.

The special conjecture that the atomic weights of the elements may be found to be whole multiples of the atomic weight of hydrogen, was for long confused with the general hypothesis that the atoms of the elements may be aggregations of the same primordial atom. The assumption is often made in memoirs on atomic weights that to prove the impossibility of expressing the atomic weights of certain elements by whole numbers, on the hydrogen scale, is to disprove the hypothesis of the primordial atom. That hypothesis can neither be proved nor disproved by determinations of the values of atomic weights.

The history of chemistry makes very clear the aid which has been given to the advance of accurate knowledge by the expression of the facts of chemical composition in terms of elements and compounds. That history also declares unhesitatingly that the only fruitful conception of element has been that which Lavoisier brought home to chemists by the uses he made of it, and Davy emphasized in the expression *undecompounded substance*. The moment any chemist has said, 'an element is a substance which cannot be decomposed,' he has found himself in slippery places.

No means has been discovered which shall determine whether a substance is absolutely undecomposable; ". . . the only difference between elements and compounds consists in the supposed impossibility of proving the so-called elements to be compounds" (Ostwald, "The Faraday Lecture," *C. S. Journal*, **85**, 520 [1904]).

Since the time of Lavoisier, the criterion of actual decomposition has been the formation from a determinate mass of a substance of two or more different substances, the mass of each of which is less than that of the original, and the sum of whose masses is equal to the mass of the original substance. As investigation has proceeded, finer means have been found for detecting minute changes of mass. The properties of radioactive substances are such that

"the quantity of those substances which can be detected is to the corresponding amount of the other elements which have to be detected by the ordinary methods of chemical analysis, in the proportion of a second to thousands of years. Thus, changes which would have to go on from almost geological epochs with the non-radioactive substances, before they become large

enough to be detected, could with radioactive substances prove appreciable effects in the course of a few hours." . . . "It is not, I think, an exaggeration to say that it is possible to detect with certainty by the electrical method a quantity of radioactive substance less than one-hundred-thousandth part of the least quantity which could be detected by spectrum analysis." [1]

In the words which I quoted on page 340, Thomson pictures the occurrence of changes in the atoms, whereby new elements are synthesized. In the phenomena of radioactivity, he finds "a very strong presumption in favour" of changes happening in the atom.[2] That the formation of a more complex from a less complex Thomsonian atom may be possible, it is necessary that the corpuscular temperature of the systems which are to combine should fall to a certain value. This decrease of corpuscular kinetic energy is accomplished by radiation; and, as the rate of radiation of these systems varies greatly with variations in the number of corpuscles, in the velocity of their motion, and in the manner of their motion, it follows that the corpuscular temperature of some atoms will be less than that of other atoms of the same elements. "Some of the atoms of any particular element will be ready to enter upon fresh changes long before the others." In making possible the existence of more stable and less stable atoms of the same element, the electrocorpuscular theory provides for the occurrence of allotropy.

A stable configuration of rotating corpuscles will become unstable when the velocity of rotation is reduced to a certain critical value; when that value is reached for atoms of special weights, there will be "a kind of convulsion or explosion, accompanied by a great diminution in the potential energy and a corresponding increase in the kinetic energy of the corpuscles [which] may be sufficient to detach considerable numbers of them from the original assemblage." The arrangement which has become unstable will give place to others which are stable, or more stable than that which has disappeared. There will be the phenomena of radioactivity.

---

[1] Thomson, *Electricity and Matter*, pp. 142, 147. I would recommend the student to read Chapter XIX "(The Ultimate Constitution of Matter and the Genesis of the Elements)" of Miss Freund's *The Study of Composition*. [1904].

[2] Thomson has recently shewn that the alkali metals give out negatively charged corpuscles, even in the dark. Hence, the atoms of these metals are probably undergoing very slight disintegration. *Phil. Mag.* (6), **10**, 584 [1905].

Assuming, for reasons which have been sketched (p. 338), that an atom of hydrogen is composed of a thousand negatively charged corpuscles, held by Faraday tubes to an equal quantity of positive electricity, and that the radius of the hydrogen atom is 10^{-8} cm., Thomson has calculated that if the energy in the atoms in one gram of hydrogen were liberated, it would be able to lift a million tons to a height considerably greater than one hundred yards. As the energy in a Thomsonian atom is greater the greater the number of corpuscles in the atom, the quantity of energy in an atom of radium, which is about 225 times heavier than an atom of hydrogen, must be enormous according to the theory we are now considering. The phenomena of radio-activity are pictured, by the theory, as causally connected with the liberation of some of this vast stock of energy, and the liberation of energy is thought of as an accompaniment of the transformations of radium, thorium, etc., into other forms of matter.

The changes which happen in radium are supposed to be connected with the breaking up of atoms, whilst ordinary chemical reactions are thought of as changes which are essentially molecular, although they are associated with the entry or the exit of corpuscles into or from the atom or the molecule.

The history of chemistry shows the importance of that classification of substances which is based on the valencies of the elements, and it brings into relief the usefulness of the division of the elements into two groups, the electropositive and the electronegative elements. How does the corpuscular atom present these classifications to us? One or more than one corpuscle may be detached from an atom by reason of the high velocities of the corpuscles, or by collisions with other atoms or with free corpuscles. An atom which loses corpuscles will be positively charged. Some atoms may readily lose one corpuscle, some two, some three, some more than three; some atoms, therefore, will acquire positive charges of one, some of two, some of three, and some of more than three units. The corpuscles in some atoms may move so slowly that one, two, or more corpuscles can be taken into the system before "the negative electrification of these foreign corpuscles forces any of the

original corpuscles out." "If the negative charge of one corpuscle were not sufficient to expel a corpuscle, while the negative charge of two corpuscles would do so, the maximum negative charge on the atom would be one unit."

The corpuscular atomic theory recognizes two classes of elements; those whose atoms are able to lose n corpuscles without taking up any foreign corpuscles, that is, electropositive elements; and those whose atoms are able to take up a greater number of foreign corpuscles than the number of home corpuscles which they lose, that is, electronegative elements. Both classes of elements are divided into groups in accordance with the valencies of their atoms. Slightly altering Thomson's words, we see that "an n-valent electropositive atom is one which, under the circumstances prevailing when combination is taking place, has to lose n corpuscles before stability is attained; an n-valent electronegative atom is one which can receive n corpuscles without driving off other corpuscles from the atom." A corpuscle which leaves an atom surrounded by good conductors will be less likely to be pulled back by the positive electrification of the atom, than it would be if the atom were isolated in space; hence, as readiness to gain or to lose corpuscles may be influenced by the circumstances of combination, "the valency of an atom may in some degree be influenced by the physical conditions under which combination is taking place."

If an atom were stable when uncharged, but became unstable by the loss, or by the gain of one corpuscle, that atom would "not be able to receive a charge either of positive or negative electricity, and [would] therefore not be able to enter into chemical combination. Such an atom would have the properties of the atoms of such elements as argon or helium."

The ordinary conception of valency is modified by the words I have quoted: "The valency of an atom may in some degree be influenced by the physical conditions under which combination is taking place." This view of valency suggests that valencies which may be called 'weaker' than the ordinary valencies of an atom may be called into play under exceptional conditions; in other words, that an atom which in most of its reactions directly combines with n other atoms may be able, under certain

special conditions, to hold to itself more than n atoms, n atoms being, perhaps, held more firmly than the others. For many years chemists have looked for a working hypothesis of this kind; they have tried to picture to themselves some kind of mechanism which should enable them to think clearly about what has been called 'potential valency,' and, less happily, 'residual affinity,' because they have known chemical facts that demand such an hypothesis as is suggested by these expressions.

In a letter to *Nature* (in 1904), Lodge [1] interpreted the corpuscular atomic theory to mean that a large number of lines of force may proceed from a corpuscle.

"When opposite charges," he said, "have paired off in solitude, . . . the bundle or field of lines constitutes a full chemical bond; but bring other charges or other pairs into the neighbourhood, and a few threads or feelers are at once available for partial adhesion in cross directions also. . . . The charge is indivisible, but the lines of force emanating from it are not indivisible or unified at all . . . quite a gradual change of valency is conceivably possible."

I doubt whether the investigation of the phenomena somewhat loosely grouped together by the term 'varying valency' will be advanced, and clearness of thinking about them encouraged, by substituting 'feelers' and 'threads' of force for 'strong and weak bonds.'

Thomson shows that the ordinary chemical method of expressing valency by *bonds* leads to results which are very like those obtained by using the electrocorpuscular theory. As an n-valent atom has n units of charge, it is pictured as the beginning, if positive, or the end, if negative, of n Faraday tubes. "Thus, if we interpret the 'bond' of the chemist as indicating a unit Faraday tube, connecting charged atoms in the molecule, the structural formulæ of the chemist can be at once translated into the electrical theory." He indicates a difference between a Faraday tube and a chemical bond, which may lead to the recognition of a very fine kind of isomerism that has not yet been noticed. No distinction can be made between the two ends of a bond; but as one end of a Faraday tube "corresponds to a positive, the other to a negative charge," there is a difference

between the two ends of the tube. If it is supposed that all the hydrogen atoms in ethane, $H-\overset{H}{\underset{H}{>}}C-C\overset{H}{\underset{H}{<}}H$, are negatively electrified, "one of the carbon atoms will have a charge of four positive units, while the other will have a charge of three positive and one negative unit, *i.e.*, two positive units; so that on this view the two carbon atoms are not in the same state." The electrical difference between a pair of carbon-atoms connected by a double bond must be greater than the difference between a pair of singly linked carbon atoms. In the molecule of ethylene, $\overset{H}{\underset{H}{>}}C=C\overset{H}{\underset{H}{<}}$, "if one carbon atom had a charge of four positive units, the other would have a charge of two positive and two negative units."

In his *Lehrbuch*, Ostwald deals with the difficulty of thinking of the atoms of an element as held together by the neutralization of positive and negative charges. If the atoms in the molecule of chlorine, for example, "are held together by the interaction of the same electrical charges as those which condition the properties of a chlorine ion, there must be positive chlorine ions besides the recognized negative chlorine ions; such are however quite unknown, *inasmuch as not one element, nor even one ion is known, elementary or compound, which is able to act both as cation and as anion.*" [1] Ostwald comes to the strange conclusion that "if the holding together of the atoms in a molecule [of an element] is dependent on electric charges, it is not those charges which obey Faraday's law."

Thomson deals with this difficulty in the latter part of Chapter V of his book. Starting with the hypothesis, which is involved in his theory "that the electrical state of an atom, depending as it does on the power of the atom to emit or retain corpuscles, may be very largely influenced by circumstances external to the atom," he shows that the more rapidly moving atoms of an elementary gas "would be more likely to lose corpuscles than the slower ones. The faster one would thus . . .

---

[1] *Lehrbuch der Allgemeinen Chemie,* ii, p. 806.

become positively electrified, while the corpuscles driven off
. . . would tend to find a home on the more slowly moving
atoms. Thus, some of the atoms would get positively, others
negatively, electrified, and those with charges of opposite signs
would combine to form a diatomic molecule."

The theory we are considering represents chemical inter-
actions to be atomic attractions which are electrical in their
origin; in this it agrees with the views expressed by Berzelius,
by Davy, and by Faraday. Whether an atom interacts chem-
ically or not depends on its "power of acquiring a charge of
electricity." To acquire a charge an atom must gain or lose
one or more than one corpuscle. As these processes are con-
ditioned chiefly by the number of corpuscles in the atom, their
motion and their configuration, there will be great differences
between the readiness of the atoms of different elements to
acquire electric charges. Atoms acquire charges of n units by
losing or gaining n corpuscles: in a mixture of n-valent atoms
capable of becoming positively charged and n-valent atoms
capable of becoming negatively charged, the corpuscles which
are lost by the former atoms will ultimately be gained by the
latter; the positively electrified atoms will attract those which
are negatively electrified, and a compound will be formed; the
change of energy will be small compared with the change which
happens when an elementary atom is disintegrating. The form of
the compound—whether it is AB, AB_2, AB_3, A_2B, A_3B, etc.—will
be conditioned by the valencies of the atoms, that is, the number
of corpuscles which each atom must gain or lose in order to be-
come stable. The formation or non-formation of the compound
will be conditioned by the readiness of the atoms, under the ex-
perimental conditions, to gain or lose those numbers of cor-
puscles which make it possible to form an atomic system that
is more stable than the original mixture of atoms; in other
words, the formation or non-formation of the compound
will be conditioned chiefly by the number, the motion, and
the configuration of the corpuscles of the atoms. We may,
perhaps, use the term *affinity* to connote the circumstances
which condition the acquirement of electric charges by the
atoms, and, therefore, the circumstances which condition the

formation of stable atomic systems. On this view, atoms combine into molecules because they become charged, positively or negatively, not because they carry positive or negative electric charges.

Atoms which acquire positive charges of electricity are the atoms of what are usually called the positive elements; if a large number of the atoms of an element are able to acquire positive charges in a short time, the element is said to be strongly positive. A certain element may be properly classed as a positive element, but it does not follow that the atoms of it will always be positively electrified in the molecules of all the compounds of the element. The distinction between positive and negative elements is very useful, but it must not be pushed too far. The quotation from *Electricity and Matter*, on pp. 347, 348, shows that the electronic theory [1] asserts the possibility of the existence of both positively and negatively electrified atoms in the same elementary gas.

A compound molecule may become unstable by physical changes in its environment, or by contact with other molecules. The molecule, as a whole, may justly be said to exhibit chemical affinity. We shall see in Chapter XIV that the affinity-constant of an acid, or of a base, is a number which determines quantitatively the reactions of the compound, and is dependent only on the composition and the constitution of it. We shall see that the affinity of an acid is changed by the substitution of positive for negative atoms, or of negative for positive atoms; the affinity of trichloracetic acid, for example, is very much greater than the affinity of acetic acid. The affinity of the atomic complex is conditioned by the affinities of its atoms; the affinities of the atoms are dependent on the number, motion, and configuration of their corpuscles, or (one may say) on the relations between the electrons and their electric charges. The relations between the electrons and their charges in a determinate atomic complex cannot be predicted from a knowledge of the general electropositive or negative characters of the atoms which form that complex. And so we come back to the fact,

---

[1] The term *electron* is more generally used than the word *corpuscle*. The electro-corpuscular theory is very often named the electronic theory.

which is announced so often and so persistently in the history of chemical inquiry, that a knowledge of the properties of elements and the properties of compounds, considered as independent entities, is very different from a knowledge of the chemical properties of elements and compounds; that the true business of chemistry is to elucidate the changes which happen in systems of homogeneous substances.

The formation of a compound is represented by the electrocorpuscular theory to be a process of the same kind as the formation of a more complex element from a simpler element. The elements are thought of as stable stages in the production of aggregations of atoms; compounds, as less stable collections of the more or less complex atoms which we call elements.

In a memoir published in 1904,[1] J. J. Thomson considers, mathematically, "the motion of a ring of n negatively electrified particles placed inside a uniformly electrified sphere," on the view that "the atoms of the elements consist of a number of negatively electrified corpuscles inclosed in a sphere of uniform positive electrification." He is led to form a picture of the negatively electrified corpuscles as arranged in a series of parallel rings inside the sphere of positive electrification, each corpuscle moving very rapidly around the circumference of the ring wherein it is situated. He shows that

"the properties conferred on the atom by this ring structure are analogous in many respects to those possessed by the atoms of the chemical elements, and that in particular the properties of the atom will depend upon its atomic weight in a way analogous to that expressed by the periodic law." "We suppose," he says, "that the mass of an atom is the sum of the masses of the corpuscles it contains, so that the atomic weight of an element is measured by the number of corpuscles in its atom."

Thomson shows that a certain arrangement of a certain number of rings will readily lose a negatively electrified corpuscle, and will thus acquire a positive charge, in other words, will act as an electropositive element; addition of more corpuscles will produce a more stable ring, an electronegative element; addition of more corpuscles will form a less stable ring, an electropositive element, and so on. The positive and negative characters, and

also the valencies, and hence the general chemical characters of the elements will vary periodically with variations in their atomic weights.

A classification of homogeneous substances which was founded on the valencies of the atoms of elements did admirable service in the quest for answers to the question, What happens when homogeneous substances interact? Although an important condition was purposely omitted from the representation which this classification gave of the constitution of molecules, nevertheless the system sufficed to cover the facts for many years. A great advance was made by the introduction, by Pasteur, of the notion of molecular asymmetry, and by the formation, by van't Hoff and by Le Bel, of a working hypothesis whereby that conception was made directly and minutely applicable to chemical reactions. Then came the ionic hypothesis, which brought with it a wider system of classification, by connecting, definitely and imaginatively, the facts of electrolytic changes with those of chemical interactions. And now we have the outlines of a system of classification which bids us think of all homogeneous substances as synthesized from "atoms . . . which are collections of positive and negative charges held together mainly by their electric attractions"; we have a system which is a development · of two conceptions, that of the atom brought home to chemists by Dalton, and that of constant electrochemical action established by Faraday. In 1836 Dumas said: "La chimie coupait les atomes que la Physique ne pouvait pas couper. Voila tout." Now the tables are turned, and it may be said that physics has cut the atoms which chemistry was content to leave undivided.

The latest form of the atomic theory is in keeping with the theoretical definition of a homogeneous substance required by the theory which certain Greek thinkers promulgated two and a half millenniums since. The definition required by that theory was, a homogenous substance is a substance composed of grains all of one kind; in place of *grains* we now say, *systems of electrical doublets*.

In a wide and loose sense, the electrical atomic theory has something in common with the alchemical device of *The One*

Thing. If for *The One Thing* we read *the primordial atomic system*, then all substances are manifestations of *The One Thing*. But, instead of saying, as the alchemists said, *The Essence* is hidden by the wrappings of specific properties which must be destroyed if *The Kernel* is to be attained, we say that the primordial atomic system is revealed by the specific properties of the substances which are the objects of our study.

CHAPTER XIII.

THE PERIODIC LAW.

SOME systems of classification of homogeneous substances have been based chiefly on the compositions, some chiefly on the reactions, and some on the connexions between the compositions and the reactions of the substances to be classified.

The sketch which I gave in Chapter VIII of the classification of acids, bases, and salts, and of compounds allied to these, showed a gradual getting nearer to the expression of reactions in terms of composition. In Chapter IX we followed the progress of the attempts to include more, and more diverse facts under a few statements of what seemed to be the essential features of the facts. These attempts found expression in the hypothesis of types, of radicals, and of electrodualism, which strengthened the proposition that similarity of reactions accompanies similarity of composition. Gradually the idea of equivalency became paramount in forming classificatory systems. I traced the development of chemical equivalency in Chapter X. That idea carried with it the notion of substitution, and gave a clearer meaning to the classification founded on types.

The fuller examination of the reactions of elements led to the recognition of facts which are expressed by the word *allotropy*; the fuller study of the reactions of compounds led to the recognition of *isomerism*. In Chapter XI I traced some of the attempts to present the facts of isomerism in terms of composition and reactions, attempts which led to the rise of structural chemistry.

As investigation advanced, more attention was given to the physical properties of systems of homogeneous substances, because the study of these properties threw light on chemical

changes. In Chapter XII were outlined the main stages in the application of electrochemical facts and ideas to the classification of elements and compounds.

In the present chapter we shall glance at some of the attempts which have been made to classify the elements, and incidentally compounds also, on the basis of the numerical relations between their atomic weights; and we shall consider the culmination of these efforts in the periodic law, a generalized statement of the connexions between composition and reactions, which gives broad answers to the two fundamental questions of chemistry, and is the foundation of the most universal of all the systems of chemical classification.

Since the establishment of the Daltonian atomic theory on a broad experimental basis by Berzelius, chemists have felt that the chemical properties of the elements, and therefore of compounds, must be connected with the values of the atomic weights of the elements. In 1829, Döbereiner tried to show that many elements may be arranged in groups of three, in each of which the middle element has an atomic weight equal, or approximately equal to the mean of the atomic weights of the two extremes.[1] In 1850, Pettenkofer attempted to prove that the differences between the atomic weights of the elements in 'a natural group' are whole multiples of a constant number.[2] In 1853, Gladstone traced "relations between the atomic weights of analogous elements," taking those elements to be analogous which were placed by Gmelin in the same group.[3]

A year after the publication of Gladstone's paper, Cooke [4] arranged the elements in series

"similar in all respects to the series of homologues of organic chemistry, in which the difference between the atomic weights of the members is a multiple of some whole number. All the elements may be classified into six

---

[1] "Versuch zu einer Gruppirung der elementaren Stoffe nach ihrer Analogie," *Pogg. Annal.*, **15**, 301 [1829].

[2] "Ueber die regelmässigen Abstände der Aequivalentzahlen der sogenannten einfackon Radicale," *Münchener Gelehrten Anzeigen*, vol. **30** [1850]. Reprinted in *Annal. Chem. Pharm.*, **105**, 187 [1858]. These two memoirs form No. 66 of Ostwald's *Klassiker der exakten Wissenschaften* [1895].

[3] *Phil. Mag.* [2], **5**, 313 [1853].

[4] "The numerical relation between the atomic weights, with some thoughts on the classification of the chemical elements," *Silliman's Amer. J.* [2], **17**, 387 [1854].

series, in each of which this number is different, and may be said to characterize its series. In the first it is nine, in the second eight, in the third six, in the fourth five, in the fifth four, and in the last three. The discovery of this simple numerical relation, which includes all others that have ever been noticed, was the result of a classification of the chemical elements made for the purpose of exhibiting their analogies in the lecture-room."

Cooke attempted to classify the elements on general chemical analogies, looking to the forms of the compounds, the conditions of their formation, and their relations to other compounds, and including the crystallographic relations, and various other physical properties of the elements and compounds. Many of Cooke's series are nearly the same as the groups obtained by applying the periodic law to the classification of elements; some of them are divided, as the groups of the periodic classification are divided, into sub-series; in some cases the same element is placed in more than one series or sub-series. In summarizing his system, Cooke said:

"I hope that I have been able to show, first, that the chemical elements may be classified in a few series similar to the series of homologues of organic chemistry; second, that in those series the properties of the elements follow a law of progression; and, finally, that the atomic weights vary according to a similar law, which may be expressed by a simple algebraic formula."

The great merits of Cooke's memoir seem to me to be that he insisted on the necessity of the comparative study of chemical facts, he showed that it is possible to arrange the elements in groups in accordance with the results of this study, and he established the existence of relations between the variations of properties of elements and compounds and the variations of the atomic weights of the elements.

In 1857,[1] Odling published a memoir entitled "On the natural groupings of the Elements," wherein he endeavoured to arrange the elements in groups in accordance with what he considered to be "the totality of their characters." At the end of his memoir Odling said:

"It is observable that we have altogether thirteen triads of similar elements, the ferric triad, and probably several others, being double from the existence of twin elements, and the platinic triad being incomplete. In each

---

[1] *Phil. Mag.* [2], **13**, 423 and 480 [1857].

triad, the intermediate term is possessed of intermediate properties, and has an exactly intermediate atomic weight. . . . Moreover, with each of several of the triads is associated an analogous element having an atomic weight approximately one-half that of the first member, or double that of the last member, of the triad."

Mention was made in the last chapter (p. 341) of Dumas' memoir, "On the equivalent weights of the simple bodies," published in 1859,[1] wherein he endeavoured to show, among other things, that the atomic weights of many similar elements are related in a very simple manner. He said:

"When one arranges in the same series the equivalents [atomic weights] of the radicals of the same family, whether in mineral or in organic chemistry, the first term determines the chemical character of all the bodies which belong to the series. . . . The type of fluorine reappears in chlorine, bromine, and iodine; that of oxygen, in sulphur, selenion, and tellurium; that of nitrogen, in phosphorus, arsenic, and antimony; that of titanium, in tin; that of molybdenum, in tungsten, etc. As if, in calling a the first term of the progression and d its ratio, one could say that in every equivalent [atomic weight] $a + n\,d$, it is a which gives the fundamental chemical character and fixes the genus, whilst $n\,d$ only determines the place in the progression and fixes the species."

Communications were made to the French Academy of Sciences in 1862 and 1863, on the classification of the elements, by Béguyer de Chancourtois. These memoirs have not been published in full; extracts and notes have appeared in *Comptes rendus* for 1862, 1863, and 1866. Under the title, *A Foreshadowing of the periodic law*, P. J. Hartog, in 1889, published in *Nature* a translation of B. de Chancourtois' first communication to the Academy, and of extracts from his other papers.[2] In 1891, Lecoq de Boisbaudran and A. de Lapparent published an account of the work of Chancourtois, with extracts from his memoirs.[3]

In the following paragraphs I have used Hartog's translation.

"On a cylinder with a circular base, I trace a helix which cuts the generating lines at an angle of 45°. I take the length of one turn of the helix as my unit of length, and, starting from a fixed origin, I mark off on the helix lengths corresponding to the different *characteristic numbers* of the system in which the number for oxygen is taken as unity. The extremities of the lines thus

---

[1] *Annal. Chim. Phys.* [3], **55**, 209 [1859].
[2] *Nature*, **41**, 186 [1889].
[3] *Compt. rendus*, **112**, 77 [1891].

marked off determine points on the cylinder which I call indifferently *characteristic points* or *geometrical characters*, and which I distinguish by the ordinary symbols for the different bodies. The same points will evidently be obtained if we take as the unit of length the one-sixteenth of a turn of the helix, and mark off on the curve lengths corresponding to the numbers of the system in which hydrogen is represented by unity."

The "characteristic numbers" used by B. de Chancourtois were "in the main the proportional numbers given by the treatises on chemistry." He, however, multiplied by two the atomic weights of many of the elements referred to hydrogen as unity, and used values which were in most cases those adopted by chemists only after they had realized the meaning of Cannizzaro's system of atomic weights, which was founded on the law of Avogadro.

"The series of points thus determined constitutes the graphic representation of my classification, which may easily be traced on a plane surface by supposing the surface of the cylinder developed. By its aid I am enabled to announce the fundamental theorem of my system: *The relations between the properties of different bodies are manifested by simple geometrical relations between the positions of their characteristic points.* . . . Simple relations of position on a cylindrical surface would be obviously defined by means of helices, of which the generating lines are only a particular case; hence, as a complement to the first theorem, we may add the following: *Each helix drawn through two characteristic points and passing through several other points or only near them, brings out relations of a certain kind between their properties; likenesses and differences being manifested by a certain numerical order in their succession, for example, immediate sequence or alternations at various periods.*"

The following "outline of the telluric helix" is taken from the paper by Lecoq de Boisbaudran and A. de Lapparent, already referred to. (See next page.)

B. de Chancourtois suggested various lines of investigation wherein his classification of the elements would point the way. He said:

"My table . . . draws up very definite programmes for the execution of several researches which are exciting attention. Will not my series, for instance, essentially chromatic as they are, be a guide in researches on the spectrum? . . . Looking at it only as a concise representation of known facts . . . the geometrical table of numerical characteristics affords a rapid method for teaching a large number of notions in physics, chemistry, mineralogy, and geology. I hope, therefore, that my natural classification of the simple bodies and radicals, being capable of rendering manifold services

ESQUISSE DE LA VIS TELLURIQUE
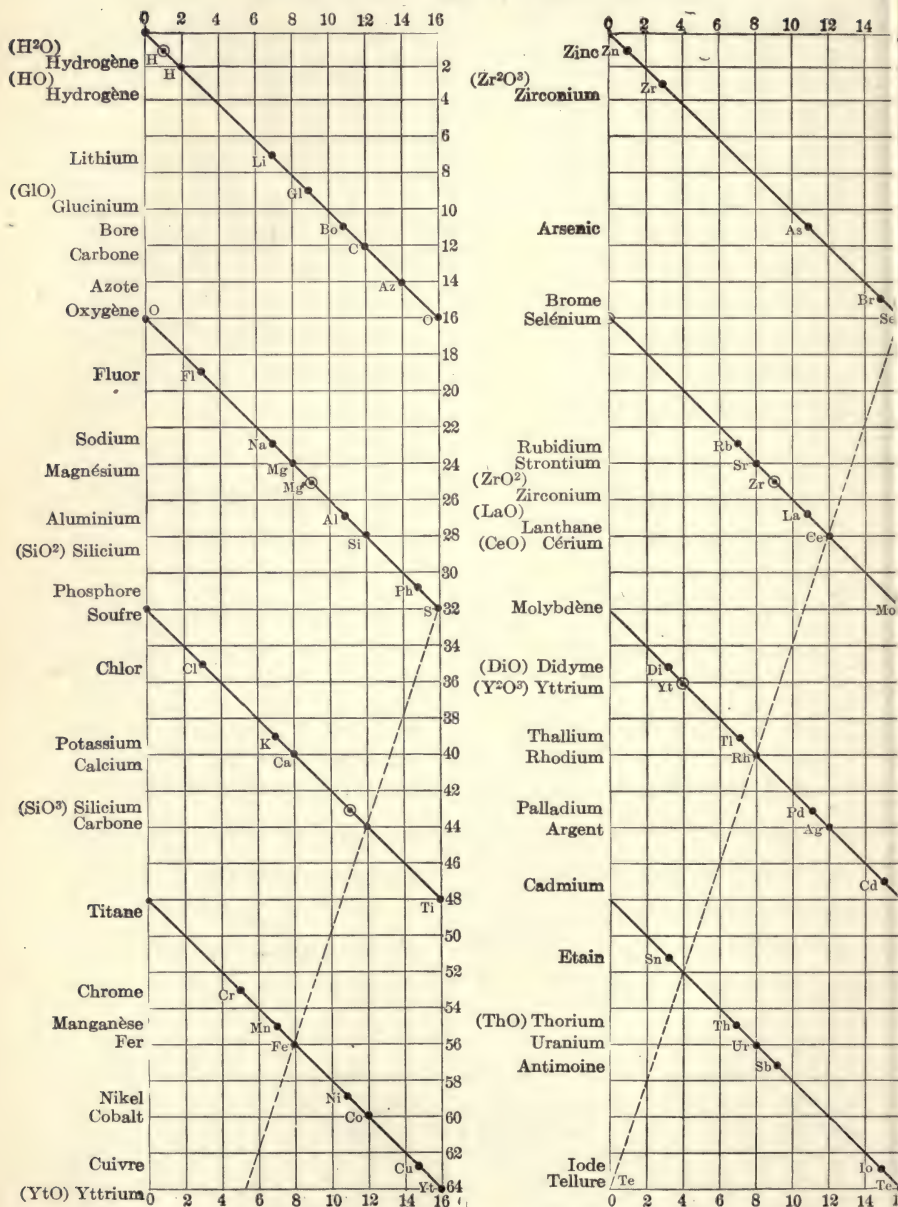
Nota.—On a entouré d'un cercle les pois correspondant aux caractères numériques dits *secondaires*

will need, like every object in habitual use, a name of easy application; hence, on account of its graphic representation and its origin, I give it the significant name of *telluric helix*. . . . The development in a plane of the cylinder ruled into squares, with the circumference at the base divided into 16 equal parts, seems to me . . . to be a *stave* on which men of science, after the fashion of musicians, will note down the results of their experimental or speculative studies, either to co-ordinate their work, or to give a summary of it in the most concise and clear form to their colleagues and the public."

In 1864, J. A. R. Newlands, independently of B. de Chancourtois, employed a musical simile in writing of the relations between the atomic weights of the elements. He said:

"The eighth element, starting from a given one, is a kind of repetition of the first, like the eighth note of an octave in music." [1]

Again:

"Members of the same group [of elements] stand to each other in the same relation as the extremities of one or more octaves in music." [2]

And once more:

"In conformity with the 'law of octaves,' elements belonging to the same group generally have numbers differing by seven, or by some multiple of seven, —that is to say, if we begin with the lowest member of a group, calling it 1, the succeeding members will have the numbers 8, 15, 22, 29, 36, etc., respectively." [3]

The "law of octaves" was proposed by Newlands as the simplest and most directly applicable expression of the relations between the atomic weights and the general chemical properties and some of the physical properties of the elements. He arranged the elements in the order of their atomic weights, using—as B. de Chancourtois had done—the values established by Cannizzaro. He asserted that if the elements are then placed in vertical lines, "with a few slight transpositions," seven elements in each line, the variation of chemical properties in a line—in an octave—is broadly like the variation of chemical properties in the other vertical lines—in the other octaves.

[1] *Chem. News*, **10**, 94 [1864].
[2] *Ibid;*, **12**, 83 [1865].
[3] *Ibid.*, **12**, 94 [1865].

The following table was shown by Newlands at a meeting of the Chemical Society on March 1, 1866:[1]

ELEMENTS ARRANGED IN OCTAVES.

	No.		No.		No.		No.		No.		No.		No.		No.
H	1	F	8	Cl	15	Co & Ni	22	Br	29	Pd	36	I	42	Pt & Ir	50
Li	2	Na	9	K	16	Cu	23	Rb	30	Ag	37	Cs	44	Os	51
G[Be]	3	Mg	10	Ca	17	Zn	24	Sr	31	Cd	38	Ba & V	45	Hg	52
Bo	4	Al	11	Cr	19	Y	25	Ce & La	33	U	40	Ta	46	Tl	53
C	5	Si	12	Ti	18	In	26	Zr	32	Sn	39	W	47	Pb	54
N	6	P	13	Mn	20	As	27	Di & Mo	34	Sb	41	Nb	48	Bi	55
O	7	S	14	Fe	21	Se	28	Ro & Ru	35	Te	43	Au	49	Th	56

In implicitly asserting the periodicity of the connexion between the atomic weights and the properties, especially the chemical properties of the elements, Newlands made a very important advance towards the most comprehensive system of classification of homogeneous substances which has been introduced into chemistry. According to L. de Boisbaudran and A. de Lapparent,[2] the sentence in italics, quoted on page 357, beginning "*each helix drawn through two characteristic points*," shows that the telluric helix of B. de Chancourtois "makes evident a true *periodicity*."

In the first edition of his *Modern Theories of Chemistry*, published in 1864,[3] Lothar Meyer arranged some of the elements in groups, on the basis of their valencies and their general chemical analogies; he indicated regularities in the differences between the atomic weights of the elements which he classified, and he left gaps between some of the elements. In 1868, Meyer extended his classification to include fifty two elements. He arranged these in fifteen groups, placing many of the elements in the order of their atomic weights, and laying special stress on the regularities in the differences between these weights. Un-

---

[1] *Chem. News*, **13**, 113 [1866]. In 1884, Newlands reprinted his papers on the law of octaves, and the notes he had communicated to *The Chemical News*, after the appearance of Mendeléeff's memoir in 1869, and published them under the title, "On the discovery of the Periodic Law and on relations among the atomic weights" [Spon, 1884].

[2] *Compt. rendus*, **112**, 79 [1891].

[3] "Die modernen Theorien der Chemie und ihre Bedeutung für die chemische Statik" [1st ed.], p. 135 [1864].

fortunately Meyer did not publish this table at the time he prepared it.[1]

Liebig's Annalen for 1870 contains a very interesting paper by L. Meyer on "The Nature of the Chemical Elements as a function of their atomic weights," written after the appearance of a brief abstract, in German, of Mendeléeff's first memoir. Meyer gives a table of the elements arranged in order of atomic weights, which, he says, is "identical in all essentials with that given by Mendeléeff,"[2] but is not borrowed from Mendeléeff's memoir.[3] He says that the "properties of the elements are, for the most part, *periodic* functions of the atomic weight;" and he exemplifies this periodic connexion in considerable detail, more especially by a curve which shows the periodic rise and fall of the atomic volumes (that is, atomic weights divided by specific gravities of the solid elements) as the atomic weights increase.

It is to Mendeléeff that chemistry owes the elucidation of the meaning of the periodic law, which states that *the properties of the elements, and the properties and compositions of compounds, vary periodically with the atomic weights of the elements.*

Mendeléeff's first memoir, "On the relations of the properties to the atomic weights of the elements," was published in 1869. His second memoir, on "The periodic regularity of the Chemical Elements," which appeared in 1871, is one of the most important contributions ever made to the advancement of accurate knowledge of natural phenomena.[4]

In the "Faraday Lecture,"[5] delivered to the Chemical Society in 1889, Mendeléeff said:

---

[1] For the history of Meyer's MS. see Ostwald's *Klassiker der exakten Wissenschaften*, No. 68, which contains the memoirs of Meyer, and also translations (into German) of those by Mendeléeff, with notes by Seubert. Those who are interested in questions of priority will find material to their liking in Seubert's notes.

[2] *Annal. Chem. Pharm.*, supplbd., 7, 354 [1870].

[3] See Meyer, *Berichte*, 13, 259 [1880].

[4] A German translation of the second memoir appeared in *Annal. Chem. Pharm.*, supplbd. 8, 133 [1871]. German translations of both memoirs, and the short German abstract of the first memoir (published in *Zeitsch. für Chemie* [2], 5, 405 [1869]), are to be found in "Das natürliche System der chemischen Elemente," which forms No. 68 of Ostwald's *Klassiker der exakten Wissenschaften* [Leipzig, 1895]. An English translation of the second memoir appeared in vols. 40 and 41 of *The Chemical News* [1879 and 1880].

[5] "The periodic law of the Chemical Elements," *C. S. Journal*, 55. 634 [1889].

"Reverting to the epoch terminating with the sixties, it is proper to indicate three series of data without the knowledge of which the periodic law could not have been discovered, and which rendered its appearance natural and intelligible. In the first place, it was at this time that the numerical values of atomic weights became definitely known. . . . Secondly, it had become evident, during the period 1860–70, and even during the preceding decade, that the relations between the atomic weights of analogous elements were governed by some general and simple laws. . . . A third circumstance which revealed the periodicity of chemical elements was the accumulation, by the end of the sixties, of new information respecting the rare elements, disclosing their many-sided relations to the other elements and to each other."

Let us now consider in some detail the two memoirs of Mendeléeff. In his first memoir, Mendeléeff sought a simple, comprehensive, and enduring basis for the classification of the elements. He passed in review the chief attempts which had been made, and found them wanting. He said:

"In all changes of the properties of the simple bodies there is *a something* which remains unchanged; in the passage of an element into compounds it is this material *something* which determines the characteristics of the compounds into which the element enters. Only one numerical value of this nature is known; it is the atomic weight peculiar to each element."

Mendeléeff began by arranging in order of atomic weights the elements whose atomic weights do not exceed 51; a periodicity was evident in the properties of these elements. He then arranged in order the elements with atomic weights greater than 100; periodicity of properties was evident there also.

"At once the thought came into my mind: cannot the properties of the elements be expressed by their atomic weights, cannot a system be based thereon?"

He then laid down the fundamental principle of the method of classification which he was about to develope.

"The atomic weight of an element determines its position in the system."

After discussing the relations between the atomic weights and the properties of the members of certain groups of chemically similar elements, Mendeléeff arranged the elements in the following table.

			Ti = 50	Zr = 90	? = 180
			V = 51	Nb = 94	Ta = 182
			Cr = 52	Mo = 96	W = 186
			Mn = 55	Rh = 104·4	Pt = 197·4
			Fe = 56	Ru = 104·4	Ir = 198
H = 1			Ni = Co = 59	Pd = 106·6	Os = 199
			Cu = 63·4	Ag = 108	Hg = 200
	Be = 9·4	Mg = 24	Zn = 65·2	Cd = 112	
	B = 11	Al = 27·4	? = 68	Ur = 116	Au = 197?
	C = 12	Si = 28	? = 70	Sn = 118	
	N = 14	P = 31	As = 75	Sb = 122	Bi = 210
	O = 16	S = 32	Se = 79·4	Te = 128?	
	F = 19	Cl = 35·5	Br = 80	I = 127	
Li = 7	Na = 23	K = 39	Rb = 85·4	Cs = 133	Tl = 204
		Ca = 40	Sr = 87·6	Ba = 137	Pb = 207
		? = 45	Ce = 92		
		?Er = 56	La = 94		
		?Yt = 60	Di = 95		
		?In = 75·6	Th = 118?		

Mendeléeff then proceeded to discuss his table; to suggest changes in some of the atomic weights then accepted; to indicate gaps to be filled up by the discovery of new elements; and generally to develope the meaning of the classification he had made.   He arrived at the following conclusions:[1]

"1. The elements, if arranged according to their atomic weights, exhibit an evident *periodicity* of properties.

2. Elements which are similar as regards their chemical properties have atomic weights which are either of nearly the same value (e.g., platinum, iridium, osmium), or which increase regularly (*e. g.*, potassium, rubidium, cæsium).

3. The arrangement of the elements, or of groups of elements in the order of their atomic weights corresponds to their so-called *valencies* as well as, to some extent, to their distinctive chemical properties—as is apparent among other series—in that of lithium, beryllium, barium, carbon, nitrogen, oxygen and iron.

4. The elements which are the most widely diffused have *small* atomic weights.

5. The *magnitude* of the atomic weight determines the character of the element, just as the magnitude of the molecule determines the character of a compound body.

6. We must expect the discovery of many yet *unknown* elements, for example, elements analogous to aluminium and silicon, whose atomic weight would be between 65 and 75.

7. The atomic weight of an element may sometimes be amended by a knowledge of those of the contiguous elements.   Thus, the atomic weight of tellurium must lie between 123 and 126, and cannot be 128.

8. Certain characteristic properties of the elements can be foretold from their atomic weights."

----

[1] I quote from Mendeléeff's words in his "Faraday Lecture" (*C. S. Journal*, **55,** 635 [1889]).

In his second memoir, after some preliminary and recapitulatory remarks, Mendeléeff discusses the nature of the periodic law. He selects elements with atomic weights from 7 to 36, arranges them in order, and uses this arrangement to illustrate the law. He pays especial attention to (1) the forms of compounds; for instance, hydrides RH, RH_2, RH_3, etc., oxides R_2O, R_2O_2, R_2O_3, etc., salts RX, RX_2, RX_3, etc., hydroxides $R(OH)$, $R(OH)_2$, $R(OH)_3$, etc.: (2) the chemical characters of the compounds whose forms he has considered; for instance, the basic or acidic characters of the oxides: (3) some physical properties of the elements; for instance, their specific gravities and atomic volumes. He then makes a similar examination of the relations between the atomic weights and the properties of other series of elements, and summarizes his results in the following statement of the periodic law.

"The properties of the elements, and, therefore, the properties of the simple, and of the compound bodies formed from them, are in periodic dependence on their atomic weights." [1]

The details of the classification he is perfecting now engage Mendeléeff's attention. His arrangement of the elements had shown that very many of them fall into *periods* each of which contains seven members, and that there are some elements which cannot be included in these seven-membered periods. He proposes to call seven elements, arranged in order of increasing atomic weights, a *short period*, or a *series*. He says:

"More marked differences are noticeable between corresponding members of even and odd series than between members of even series, or of odd series. An example makes this sufficiently obvious:

"Fourth series:	K	Ca	—	Ti	V	Cr	Mn.
Fifth series:	Cu	Zn	—	—	As	Se	Br
Sixth series:	Rb	Sr	—	Zr	Nb	Mo	—
Seventh series:	Ag	Cd	In	Sn	Sb	Te	I.

The similarity between the members of the fourth and sixth series is more marked than that between them and the members of the fifth or of the seventh series."

---

[1] The expression *simple bodies . . . formed from the elements* is used by Mendeléeff in order to include the allotropic forms of elements.

Those elements which cannot be included in the short periods are placed between the last member of an even series and the first member of the next odd series, and form an eighth group. This leads to the recognition of *long periods*, each containing seventeen members.

The members of the eighth group are these:

$$
\begin{array}{ccc}
\text{Fe} & \text{Ni} & \text{Co} \\
\text{Ru} & \text{Rh} & \text{Pd} \\
\text{Os} & \text{Ir} & \text{Pt}
\end{array}
$$

After discussing in detail the properties and relations of these nine elements, Mendeléeff gives two tables, "for the better explanation of what has been said." In the first table, the elements are arranged in long periods; in the second table, they are placed in groups and series, and the difference between even series and odd series is plainly indicated. The following is Mendeléeff's first table; the second is given on p. 366.

TABLE I.

Typical Elements.							
			K =39	Rb = 85	Cs =133	—	—
			Ca =40	Sr = 87	Ba =137	—	—
			—	?Yt = 88?	?Di =138?	Er =178?	—
			Ti =48?	Zr = 90	Ce = 140?	?La =180?	Th =231
			V =51	Nb = 94	—	Ta =182	—
			Cr =52	Mo = 96	—	W =184	U =240
			Mn =55	—	—	—	—
			Fe =56	Ru =104	—	Os =195?	—
			Co =59	Rh =104	—	Ir =197	—
H=1			Ni =59	Pd =106	—	Pt =198?	—
	Li = 7	Na =23	Cu =63	Ag =108	—	Au =199?	—
	Be= 9·4	Mg =24	Zn =65	Cd =112	—	Hg =200	—
	B =11	Al =27·3	—	In =113	—	Tl =204	—
	C =12	Si =28	—	Sn =118	—	Pb =207	—
	N =14	P =31	As =75	Sb =122	—	Bi =208	—
	O =16	S =32	Se =78	Te =125?	—	—	
	F =19	Cl =35·5	Br =80	I =127	—	—	

Atomic weights are given in round numbers. A note of interrogation before the symbol of an element means that the position of this element in the system cannot be regarded as determined. A note of interrogation after the atomic weight of an element means that the value of the atomic weight is doubtful, because the equivalent has not yet been determined with sufficient accuracy.

Copper, silver, gold are included in the eighth group, because of their analogies with the other members of

TABLE II.

Series.	Group I. R^2O	Group II. RO	Group III. R^2O^3	Group IV. RH^4 RO^2	Group V. RH^3 R^2O^5	Group VI. RH^2 RO^3	Group VII. RH R^2O^7	Group VIII. RO^4
1	H = 1							
2	Li = 7	Be = 9·4	B = 11	C = 12	N = 14	O = 16	F = 19	
3	Na = 23	Mg = 24	Al = 27·3	Si = 28	P = 31	S = 32	Cl = 35·5	
4	K = 39	Ca = 40	— = 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56 Co = 59 Ni = 59 Cu = 63.
5	(Cu = 63)	Zn = 65	— = 68	— = 72	As = 75	Se = 78	Br = 80	
6	Rb = 85	Sr = 87	?Yt = 88	Zr = 90	Nb = 94	Mo = 96	— = 100	Ru = 104 Rh = 104 Pd = 106 Ag = 108
7	(Ag = 108)	Cd = 112	In = 113	Sn = 118	Sb = 122	Te = 125?	I = 127	— —
8	Cs = 133	Ba = 137	?Di = 138	?Ce = 140	—	—	—	— —
9	(—)							
10			?Er = 178	?La = 180	Ta = 182	W = 184	—	Os = 195 Ir = 197 Pt = 198 Au = 199
11	(Au = 199)	Hg = 200	Tl = 204	Pb = 207	Bi = 208	—		— —
12	—	—	—	Th = 231	—	U = 240	—	— —

this group; if attention is paid to the form of their lower oxides, these metals may be placed in the first group also along with the alkali metals.

Mendeléeff considers, very fully and in much detail, the resemblances and differences between elements in even series and those in odd series; the peculiar relations, as regards both atomic weights and properties, between those elements he calls *typical* and the other elements; the gradation of properties in long periods, in short periods, and in some of the groups; and other questions concerning the relations of atomic weights to properties which can be elucidated by the help of the periodic law. He then says:

"Every natural law acquires scientific importance only when it, so to say, makes possible practical deductions, that is, when it allows logical conclusions to be drawn which explain the unexplained, and point to phenomena unknown before, and especially when the law calls forth predictions which can be experimentally verified. In such a case, the utility of the law is obvious, and it is possible to prove its correctness. Such a law will certainly incite to the elaboration of other parts of science. I will, therefore, more narrowly consider some deductions from the periodic law, and in particular the applications of it to the following purposes:

To systematizing the elements.

To determining the atomic weights of elements which have not been sufficiently examined.

To considering the properties of elements as yet unknown.

To correcting the values of atomic weights.

To completing our knowledge of the forms of chemical compounds."

Mendeléeff divides all the systems which have been used for classifying the elements into two groups: *artificial* systems and *natural* systems. The artificial systems rest on one, or on a few characteristics; elements are classed according to their affinities, their electrochemical behaviours, their valencies, their physical properties, and so on. The natural systems divide the elements into groups in accordance with their chemical analogies. But these analogies are sometimes very vague, sometimes they almost disappear; the same element is placed in more than one group; the groups are not simply related to one another; there is a lack of unity in every one of the schemes. The periodic law makes it possible to form a complete system free from every kind of arbitrariness.

"The position of an element R in the system is determined by the series and the group to which R belongs, also by the elements X and Y which come next to R in the same series, and also by the two elements in the group with the next smaller atomic weight (R′) and the next greater atomic weight (R″). The properties of R may be determined from the known properties of X, Y, R′, and R″. . . . I call the relations of R to X and Y on the one hand, and to R′ and R″ on the other hand, the *atomic analogies* of the element. Thus. As and Br on the one hand, and S and Te on the other hand, are atomic analogues of Se. whose atomic weight has the mean value of $78 = \left(\dfrac{75+80+32+125}{4}\right)$; hence, the properties of SeH_2 show that this compound comes midway between AsH_3–BrH and SH_2–TeH_2; and so on. The relations of atomic analogies are not completely valid in the end-series and end-groups. although here also may be observed definite mutual relations which can be conditionally expressed by arithmetical (not by geometrical) proportions; for example, $X′:X=R′:R=Y′:Y$, or $X′:R′=X:R=X″:R″$, and so forth."

Mendeléeff illustrates the use of the periodic law in systematizing the elements by discussing very fully, on the lines laid down in the sentences I have quoted, the positions to be given to beryllium, vanadium, and thallium.

In considering the application of the law to determining the atomic weights of elements which have not been sufficiently examined, Mendeléeff sketches the different methods available for determining atomic weights, and concludes that there are only two methods of general applicability; that based on estimations of the vapour-densities of many compounds of an element, and that which rests on comparisons of the chemical properties of an element with those of other elements which have been more thoroughly investigated. The periodic law is very helpful when the second of these methods is used.

"Let E be the equivalent of an element determined from the composition of its highest oxide (the composition of the oxide is E_2O, and of the chloride $E\,Cl$); then the possible values of the atomic weight of the element are obtained by multiplying E by 1, 2, 3, 4, 5, 6, 7. The true atomic weight of the element is that one of the possible values, call it E_n, which corresponds to an unoccupied place in the system, and at the same time answers the requirements of the atomic analogies of the element."

Mendeléeff illustrates the foregoing statement by discussing the atomic weight of an element which has the equivalent weight 38, and forms an oxide that is not very strongly basic

and does not combine with more oxygen. If the atomic weight of the element is 38, its oxide is R_2O, and it must be placed in the first group. But the possible place is occupied by $K = 39$, an element whose oxide is a soluble and energetic base. If the oxide is RO, then $R = 76$, and the element must be assigned to the second group. But $Zn = 65$, and $Sr = 87$, and there is no place for an element with an atomic weight between these two values. If the oxide is R_2O_3, then $R = 114$, and the element belongs to the third group. There is a place, between $Cd = 112$ and $Sn = 118$, for an element with an atomic weight equal to about 114. Judging from the atomic analogies with Al_2O_3 and Tl_2O_3, and also from those with CdO and SnO_2, the oxide R_2O_3 must have a feebly basic character. Hence the element is to be placed in the third group. The element R cannot find a place in the fourth group, because if it is put into that group its oxide must be RO_2 and its atomic weight 152, and the unoccupied position in the fourth group must be filled by an element with the atomic weight of 162, and having a feebly acidic oxide which shall serve as a stepping stone from PbO_2 to SnO_2. An element with the atomic weight 152 might find a place in the eighth group; but the characteristics of this element, which would come between Pd and Pt, would be so marked that they could not be overlooked; and if the element R does not possess these characteristics, it cannot have the atomic weight 152, nor can it find a home in the eighth group. If the oxide of R is R_2O_5, then $R = 190$; but there is no vacancy for this element in the fifth group, because $Ta = 182$, and $Bi = 208$, and the oxides Ta_2O_5 and Bi_2O_5 are somewhat acidic. The oxide-forms RO_3 and R_2O_7 will not fulfil the requirements of the element we are considering. Hence the only possible value for the atomic weight of R is 114, and the only possible formula for its oxide is R_2O_3. The element whose atomic weight is being determined is indium. Mendeléeff then proceeds to discuss in detail the atomic analogies of indium. He comes to the conclusion that the composition of the oxide of indium must be In_2O_3, and the atomic weight of the element must be about 114. When Mendeléeff wrote, the atomic weight of indium was supposed to be about 75, and the metal was supposed to form the oxide InO.

The analogies between uranium and other elements are discussed very fully by Mendeléeff; he shows that the atomic weight of 120 assigned to this element in 1870 must be doubled, and the formulæ of its compounds changed. He places uranium in the twelfth series and the sixth group, and suggests many investigations which should be made. Most of these investigations have been made; their results have entirely justified Mendeléeff's correction of the atomic weight of uranium.

The positions in the classificatory scheme of cerium, didymium, erbium, lanthanum, and yttrium are discussed by Mendeléeff in the light of the periodic law; changes are suggested, and lines of investigation are sketched.

After drawing attention to the existence of vacant places in his periodic arrangement of the elements, Mendeléeff says:

"I will describe the properties of some elements whose discovery is to be expected, in order to help the attainment of a new proof of the justness of the periodic law, a proof which is very definite, although it will be realized only in the future. . . . To avoid the introduction into science of new names for unknown elements, I propose to designate such elements by adding numerical Sanskrit prefixes (eka, dvi, tri, tschatur, etc.) to the names of the next lower analogous elements of the even or odd series of the same group. Thus, the unknown elements of the first group will be called ekacæsium, $Ec = 175$, and dvicæsium, $Dc = 220$. Were niobium unknown, it would be called ekavanadium."

Mendeléeff, then, using the method already illustrated by the account given on pages 368, 369, of his study of the atomic analogies of indium, determines the properties of three unknown elements: *ekaboron*, an element to be placed in the fourth series of the third group, with the atomic weight $Eb = 44$; *ekaaluminium*, $Ea = 68$, to be placed in Group III, series 5; and *ekasilicon*, $Es = 72$, which will find its proper place next but one to silicon in Group IV. The predictions made by Mendeléeff are not slight sketches, but full, clear, and detailed descriptions of the properties, and of the chemical relations of the three elements. His predictions have been completely verified by the discovery, and the elucidation of the properties and relations of scandium (*ekaboron*), gallium (*ekaaluminium*), and germanium (*ekasilicon*).

In his " Faraday Lecture," delivered to the Chemical Society

in 1889,[1] referring to the discovery of gallium, scandium, and germanium, Mendeléeff said:

"When, in 1871, I described to the Russian Chemical Society the properties, clearly defined by the periodic law, which such elements ought to possess, I never hoped that I should live to mention their discovery to the Chemical Society of Great Britain as a confirmation of the exactitude and the generality of the periodic law. Now that I have had the happiness of doing so, I unhesitatingly say that although greatly enlarging our vision, even now the periodic law needs further improvements in order that it may become a trustworthy instrument in further discoveries."

In a foot-note to the sentence just quoted,[2] Mendeléeff said:

"I foresee some more new elements, but not with the same certitude as before. I shall give one example, and yet I do not see it quite distinctly. In the series which contains $Hg = 200$, $Pb = 206$, and $Bi = 208$, we can guess the existence (at the place VI—11) of an element analogous to tellurium, which we can describe as dvi-tellurium, Dt, having an atomic weight of 212, and the property of forming the oxide DtO_3."

He then describes some other properties of dvitellurium. The more accurate are the determinations of atomic weights, the more is it evident that the differences between the atomic weights of corresponding elements in the periodic classification are approximately equal, but, at the same time, the more noticeable are the individual *deviations* from the average differences.

"Hence, there must be certain general properties of the elements (such as the ability to give definite oxidation-forms, which changes step by step) that are in periodic dependence on the atomic weights, and there must be individual properties that are conditioned by the *deviations* which have been mentioned. Inasmuch as, at present, we know only that the relation in question is periodic, but it itself remains unknown, we have no means of determining the magnitude of the deviations, and therefore no means of applying an exact correction to the values of atomic weights; we can only lay down narrow *limits* within which the value of the atomic weight of an element under discussion must fall."

The atomic weight of tellurium is discussed by Mendeléeff; he asserts that it must be greater than that of antimony, given by him as 122, and smaller than that of iodine, which he takes as 127. He indicates some of the difficulties in determining the

---

[1] *C. S. Journal*, **55**, 634 [1889].
[2] *Ibid.*, **55**, foot-note to p. 649.

atomic weights of platinum, iridium, and osmium, and comes to
the conclusion that the order of the atomic weights of these
elements which was generally accepted when he wrote should
be reversed, that the atomic weight of platinum is the largest
of the three, and that of osmium is the smallest.

Mendeléeff treats at considerable length the subject of the
application of the periodic law to completing our knowledge of
the forms of chemical compounds. He objects to the great
prominence which had been given to the doctrine of valency.
"It is the fate of our science," he says, "that the most important
discoveries of an epoch lead at first to extreme hypotheses."
The applications of that doctrine to the compounds of carbon
had produced great results; because, according to Mendeléeff,
carbon is quadrivalent towards both hydrogen and oxygen, and
the compounds of carbon do not tend to form molecular com-
pounds. But, he says, "conclusions which are perfectly ap-
plicable to carbon compounds are not trustworthy when applied
to compounds of other elements."

"There are three main propositions which give stability to all repre-
sentations of chemical structure. I will formulate them tentatively as
follows. *The principle of substitution.*—When any molecule is separated into
two parts, both parts are equivalent to one another (they can replace one
another). . . . Therefore H_2 and O are equivalent, HO–H, CH_3–H, CH_2–H_2,
C–H_4, Cl–H, K–Cl, and consequently K–H, NH_2–H, NH_4–Cl or H or K, and so
forth. . . . *The principle of limits.*—When a molecule breaks down, at
least one of the molecules which are formed can combine with such a quantity
of elements as is equivalent to the second molecule which was produced by
the falling to pieces of the original molecule. Hence, C_2H_4, which is formed
by the elimination of a molecule of H_2O from C_2H_6O, can combine with Cl_2
(equivalent to H_2O), with HCl, etc. . . . *The periodic principle.*—The
highest compounds of an element with hydrogen and oxygen, hence, also with
equivalent elements, are determined by the atomic weight of the element,
whereof they are a periodic function."

Mendeléeff says that his presentation of the forms of com-
pounds of the elements with hydrogen shows no essential differ-
ences from that which is based on the doctrine of valency; but
he declares that important differences are apparent between the
two systems when compounds other than hydrides are con-
sidered. Comparing the oxide-forms R_2O, RO, R_2O_3, RO_2,
R_2O_5, RO_3, R_2O_7, and RO_4 with the hydride-forms RH, RH_2,

RH_3, and RH_4 (which is the limiting form for hydrides), Mendeléeff says that, as eight is the sum of the hydrogen and oxygen equivalents which one elementary atom can hold, those elements which give RO_4 form no hydrides, those which are able to form R_2O_7 give RH, those which give RO_3 give also RH_2, those which give R_2O_5 give also RH_3, and those whose oxide-form is RO_2 form hydrides RH_4.

"The formation of complex saline oxy-compounds is determined by the form of the simple oxygen-compounds; for example, there may be replacement of O in the hydrates by equivalent quantities of $(HO)_2$, or of H_2. Hence, $SO_2(OH)_2$, $SO_2H(OH)$, and SO_2H_2 will be formed from SO_3. From CO_2 arise $CO(OH)_2$, $COH(OH)$, and COH_2. . . . The lower forms of compounds may change into the highest possible forms indirectly, or by direct addition. If RX_n is the highest form of the compounds of an element R, a determinate form RX_{n-m} will pass to the limiting form, RX_n, by taking up X_m, or equivalent quantities of other substances."

The limiting forms of haloid compounds are never higher, but are often lower than those of the corresponding compounds with oxygen.

"The capacity which many elements, but not all elements possess of giving different compound-forms, finds its full expression neither in the hydrogen-compounds nor in the highest forms of oxygen-compounds, especially when the compounds consist of more than two elements. Whole molecules may combine to produce higher forms: polymeric and so-called molecular compounds. Thus, the complete capacity of Si to form compounds is not expressed by the form SiX_4 (corresponding to SiH_4, SiO_2, $SiCl_4$). For Si produces $SiO_2 nSiO_2$, $SiF_4 2HF$, etc., besides SiO_2. Besides PtO_2, $PtCl_4$, or generally PtX_4 and PtX_2, platinum gives also $PtX_4 nA$, where A signifies a complete molecule and n is generally a whole number; for example, $PtCl_2 2RCl$, $PtCl_4 8H_2O$, $PtCl_4 2HCl6H_2O$, $PtX_2 2NH_3$, $PtX_2 4NH_3$, $Pt2HCy5H_2O$, $PtCy_2 MgCy_2 7H_2O$, and other similar compounds. Some of these compounds are very stable, take part in double decompositions, and are known for many elements. . . . Those compound-forms serve to characterize some elements (for instance, the alum-forms, the forms of many salts, $RSO_4 7H_2O$, $RK_2(SO_4)_2 6H_2O$, and the like); hence, they deserve as close a comparative study as all other forms, from which, indeed, they do not essentially differ. . . ."

"In the foregoing exposition I have endeavoured to found myself on the law of substitution, the law of limits, and the periodic law, and I am of opinion that all generalizations concerning the forms of compounds of the elements must rest upon these laws. . . ."

"Among the data which are required for the characterization of an element two are essential, and these are obtained by collecting and comparing the results of observation and of experiment; the two data are, the definite

atomic weight and the definite valency. As the periodic law brings into relief the interdependence of these two magnitudes, it also makes possible the determination of one from the other, namely, the valency from the known atomic weight, and therefore, if the doctrine of valency determines the forms of compounds, the periodic law also determines these forms; but the latter goes somewhat further, inasmuch as it also determines those oxygen-forms which remain outside the attention of the doctrine of valency."

Mendeléeff illustrates the foregoing statements by a detailed examination of the forms of the compounds of boron and of aluminium.

Many memoirs on subjects conected with the periodic law have appeared since 1871; several deal with the positions to be assigned to individual elements, and the relations of individual elements to their analogues; some attempt to modify the presentation of the law as it appears in Mendeléeff's tables.[1] But Mendeléeff's memoir of 1871 remains the foundation, and also the elucidation of the periodic classification of homogeneous substances. That memoir should be studied in detail by every one who desires to know what the periodic law is, and what it does for chemical classification. I would advise students also to read with care and thought Mendeléeff's " Faraday Lecture " delivered in 1889,[2] and his pamphlet *An attempt towards a Chemical conception of the ether*, which was published in 1904.[3] The latter contains Mendeléeff's views regarding the positions to be given in the periodic system to the inert elements argon, helium, krypton, neon, and xenon.

I would ask the student to notice that the electrocorpuscular theory of the structure of atoms leads to the recognition of a periodic connexion between the atomic weights and the properties of the elements (see Chapter XII, p. 350).

If it is possible to express all the essential relations between the compositions and the properties of homogeneous substances in a single brief statement, the full meaning of that statement will not be realized until it has been applied to many facts unnoticed when it was made. A generalized expression of the re-

---

[1] An account of the most important of these memoirs will be found in Miss Freund's *A Study of Chemical Composition*, pp. 483–505[1904]. See also Werner, *Berichte*, **38**, 914 [1905].

[2] *C. S. Journal*, **55**, 634 [1889].

[3] Longmans & Co., 1904.

ıations between the vast concourse of facts and ideas called up in the mind by the words *composition* and *reactions* must be not only comprehensive and exact, but also imaginative and inexhaustible. Only a man of genius could attain to it.

The future will decide whether the periodic law is the long looked for goal, or only a stage in the journey, a resting-place while material is gathered for the next advance.

THE HISTORY OF THE STUDY OF THE CONDITIONS AND GENERAL LAWS OF CHEMICAL CHANGE.

INTRODUCTORY REMARKS.

In Part I of this book I endeavoured to fix the attention of the reader on what seem to me to be the most important steps in the development of the idea of homogeneous substances. Lavoisier described chemical changes as the interactions of elements and of compounds, and gave exact meanings to the words *element* and *compound*.

Dalton presented chemistry with the key which opened the door into a land that had been vaguely seen long before, and made plain the high roads of that land, roads wherein many "a wayfaring man, though a fool," has walked without greatly stumbling. A vast, vague universe of atoms was imagined by the Greek thinkers; after two thousand years a few pages in a small book began the transformation of that "world not realized" into the finest and most powerful instrument of exact thought which physical science has constructed.

The imaginings of chemists became gradually truer pictures of natural happenings. The atom was distinguished from the molecule. Facts which seemed outside the grasp of the generalizations of chemistry found expression in terms of the atomic and molecular theory. Allotropy was explained. The idea of element and of compound was widened, and, at the same time, made more exact.

376

The processes of extension and intensification were accomplished by studying the connexions between the compositions and the reactions of homogeneous substances. Some of the steps in the development of the study of these interactions have been described in the first section of Part II of this book. Many lines of investigation gradually converged. The hypotheses of radicals and types found a common ground of support in the facts of chemical equivalency, and both hypotheses were included in the wider conception of the dependence of chemical properties on the nature, number, and arrangement of the atoms which are the undivided parts of molecules. Structural chemistry began. The number of new facts discovered by using the conception of molecular structure as a guide was enormous. Chemists staggered under the burden of facts. But men of genius appeared who delivered them from the tyranny by widening and clarifying the fundamental idea, drawing with a bolder and a finer hand the picture of the molecule as an orderly assemblage of parts.

Then a new world was discovered. The indivisible atom was shattered. But the atomic theory remained. Vast possibilities are half revealed and half concealed. Enormous stores of energy are being discovered in those complex systems of almost infinitely minute particles which we used to think were the ultimate building stones of the universe. Nevertheless it is those complex systems, which we still call atoms, that determine the chemical characters of the elements and their compounds. The periodic law, which tells that the properties of the elements and the properties and compositions of the compounds are periodic functions of the atomic weights of the elements, remains as the sure foundation of the one general system of chemical classification.

Chemistry is the systematic and comparative study of the changes which happen in systems of homogeneous substances. Hitherto our attention has been concentrated on the main lines along which advance has been made in the elucidation of the changes of composition and the changes of chemical properties of these systems. We must now look to the progress of the study of the general conditions of chemical change. We must

try to draw broadly the outlines of the development of chemical affinity and chemical equilibrium; and we must glance—we can do no more than glance — at the history of the new branch of science which is being constructed and is called physical chemistry.

CHAPTER XIV.

CHEMICAL AFFINITY.

To the third chapter of his book on *Opticks* (published in 1701) Newton attached a number of queries. In the thirty-first query we read:

"Have not the small Particles of Bodies certain Powers, Virtues, or Forces, by which they act at a distance . . . upon one another for producing a great part of the Phænomena of Nature? For it's well known that Bodies act upon one another by the Attractions of Gravity, Magnetism, and Electricity; and these Instances show the Tenor and Course of Nature, and make it not improbable but that there may be more attractive Powers than these. . . . How these Attractions may be perform'd, I do not here consider. What I call Attraction may be perform'd by impulse, or by some other means unknown to me. I use that Word here to signify only in general any Force by which bodies tend towards one another, whatsoever be the Cause. For we must learn from the Phænomena of Nature what Bodies attract one another, and what are the Laws and Properties of the Attraction, before we enquire the Cause by which the Attraction is perform'd. The Attractions of Gravity, Magnetism, and Electricity, reach to very sensible distances, and so have been observed by vulgar Eyes, and there may be others which reach to so small distances as hitherto escape Observation. . . ."

"When Oil of Vitriol is mix'd with a little Water, or is run *per deliquium*, and in Distillation the Water ascends difficultly, and brings over with it some part of the Oil of Vitriol in the form of Spirit of Vitriol, and this Spirit being poured upon Iron, Copper, or Salt of Tartar, unites with the Body and lets go the Water, doth not this show that the acid Spirit is attracted by the Water, and more attracted by the fix'd Body than by the Water, and therefore lets go the Water to close with the fix'd Body? . . . And is it not also from a natural Attraction that the Spirits of Soot and Sea-Salt unite and compose the Particles of Sal-ammoniac . . . and that the Particles of Mercury uniting with the acid Particles of Spirit of Salt compose Mercury Sublimate, and with the Particles of Sulphur, compose Cinnaber . . . and that in subliming Cinnaber from Salt of Tartar, or from quick Lime, the Sulphur by a stronger Attraction of the Salt or Lime lets go the Mercury, and stays with the fix'd Body . . . ?"

After giving many more examples of chemical actions, Newton says:

"The parts of all homogeneal hard Bodies which fully touch one another, stick together very strongly.   And for explaining how this may be, some have invented hooked Atoms, which is begging the Question; and others tell us that Bodies are glued together by rest, that is by an occult Quality, or rather by nothing; and others, that they stick together by conspiring Motions, that is by relative rest amongst themselves.   I had rather infer from their Cohesion, that their Particles attract one another by some force, which in immediate Contact is exceeding strong, at small distances performs the chymical Operations above mention'd, and reaches not far from the Particles with any sensible Effect."

Having considered various phenomena, and referred them to attractions of different kinds, Newton says:

"And thus Nature will be very conformable to her self and very simple, performing all the greater Motions of the heavenly Bodies by the Attraction of Gravity which intercedes those Bodies, and almost all the small ones of their Particles by some other attractive and repelling Powers which intercede the Particles."

The assertion that *like attracts like* was made by some of the Greek thinkers four or five hundred years before Christ, and was the basis of most of the alchemical writings on the cause of chemical reactions.   The statement that substances which unite to form things different from themselves contain some common principle or essence, was translated by the alchemists into their symbolic language; they said that a substance unites only with those it loves and desires to be with, only with those which are related to it by the bonds of natural affinity.

Boyle (last quarter of the seventeenth century) combated the alchemical method of expressing the reactions of material things in terms which should be applied only to intelligent beings.   In his *Reflections upon the Hypothesis of Alcali and Acidum*, Boyle says:

"I look upon amity and enmity as affections of intelligent beings, and I have not yet found it explained by any, how those appetites can be placed in bodies inanimate and devoid of knowledge or of so much as sense.   And I elsewhere endeavour to show, that what is called sympathy and antipathy between such bodies does, in great part, depend upon the actings of our own intellect, which supposing in everybody an innate appetite to preserve itself both in a defensive and an offensive way, inclines us to conclude, that that body, which though designlessly, destroys or impairs the state or texture of another body, has an enmity to it, although perhaps a slight mechanical change may make bodies, that seem extremely hostile, seem to agree very well and co-operate to the production of the same effect."

In the middle of the eighteenth century, Boerhave spoke of the affinity of a substance for others which are unlike it, and impressed on the term *affinity* the meaning which it has retained since his time, namely, the force that holds together chemically dissimilar substances. This meaning was emphasized and made more exact by Newton, whose view that the affinities of substances were the results of attractions acting at insensible distances between very minute particles, was followed by most of the chemists of the eighteenth century.

How are these affinities, these attractions, to be measured?

Many of the alchemists noticed that one substance will often turn out another from certain of its compounds. In the middle of the seventeenth century, Glauber recorded reactions wherein a substance which had turned out another from compounds thereof was itself expelled by a third substance from the compounds which it had produced. The more careful and fuller examination of such reactions led to the formation of *tables of affinity*, which were the answers given by chemists of the eighteenth century to the question, How are affinities to be measured?

The most celebrated of the older tables of affinity was that published by Geoffroy early in the eighteenth century.[1] It is reproduced on page 382.

Each vertical column contains substances arranged in the order of what Geoffroy took to be their affinities for the substance at the head of the column. Geoffroy said that no substance in a column could be expelled from its compound with the substance at the head of that column by any one of the substances placed below it in the column, and that a substance was able to expel any other placed below it from the combination of that other with the substance at the head of the column.

If A turns out B from the combination BC, and forms the combination AC, then, according to Geoffroy, the affinity of A for C is greater than that of B for C; in other words, the force of attraction between A and C is greater than that between B and C. If Geoffroy's assumptions are accepted, his table is

---

[1] " Table des différents rapports observés en Chimie entre différentes Substances," par M. Geoffroy l'aîné, *Mém. de l'Acad. des Sciences* for 1718, p. 202.

TABLE DES DIFFÉRENTS RAPPORTS.

OBSERVÉS ENTRE DIFFÉRENTES SUBSTANCES.

🜊 Esprits acides.
Acide du sel marin,
Acide nitreux.
Acide vitriolique.
Sel alcali fixe.
Sel alcali volatil.

▽ Terre absorbante.
SM Substances metalliques,
☿ Mercure.
♕ Regule d'Antimoine.
☉ Or.
☽ Argent.

♀ Cuivre.
♂ Fer,
♄ Plomb.
♃ Etain.
♋ Zinc
PC Pierre Calaminaire.

△ Soufre mineral. [Principe.
🜊 Principe huileux ou Soufre
▽ Esprit de vinaigre. [Eau.
⊖ Sel.
▽ Esprit de vin et Esprits ar-[dents

an expression, but not a numerical expression of the relative affinities of certain substances.

In his book on affinity, published in 1777, Wenzel [1] came to a conclusion different from that expressed in Geoffroy's table. Wenzel's argument proceeded somewhat as follows. When several substances dissolve in, and combine with a common solvent, we ought to think of the substances as different loads, and of the common solvent as a force which acts more quickly, or more slowly, on one substance than on another. Hence, Wenzel concluded that the quicker the action of the solvent the greater was the degree of its affinity—"the affinity of substances for a common solvent is inversely as the times required for solution."

Wenzel described experiments which he made with equal-sized cylinders of different metals, covered with varnish except on one surface of each, and immersed in the same solvent, at the same temperature, for equal times. From the weights dissolved in a determinate time, he calculated the times required for the solution of each cylinder. The differences between the times required for the solution of the various cylinders were taken by Wenzel to express the differences of the affinities of the metals for the solvent. The results seemed simple. But Wenzel found that other experiments led to contradictory conclusions. He discussed several instances of reactions between two compounds which produced two other compounds, and came to the general conclusion that chemical changes must be thought of as the results of various actions and reactions which balance one another. He spoke of the combination of A with B, A with D, B with C, B with D, etc., as forces; one force, he said, may be greater than another, and yet be smaller than the sum of all the others.

Wenzel's general result might be expressed by saying that under certain circumstances the affinity of A for B is greater than that of C for B, but under other circumstances the affinity of C for B is greater than that of A for B.

---

[1] The edition I have consulted was published in 1800; it is entitled *Carl Friedrich Wenzels Lehre von der Verwandtschaft der Körper mit Anmerkungen, herausgegeben von David Hieronimus Grundel.* Dresden, bey Heinrich Gerlach, 1800.

We shall see what great effects on the study of chemical affinity have been produced by realizing the conception of balanced actions, and that of the modifying influence of various conditions on affinity, conceptions which were first used by Wenzel.

Geoffroy's table was based on the assumption that the order of the affinities of substances for one and the same substance is constant. The constancy of the order of affinities was emphatically declared by Bergmann, whose dissertation on affinity [1] was accepted as authoritative by most chemists for many years from about 1775.

Bergmann distinguished *affinity of aggregation*, which is exhibited, he said, when homogeneous substances unite so that there is only an increase of mass, from *affinity of composition*, which comes into action when heterogeneous substances are mixed and form combinations. He also differentiated *single elective attraction* from *double attraction*. The union of two out of three substances, to the exclusion of the third, he designated *single elective attraction;* the change of constituents by two compounds, each consisting of "only two proximate principles," he called *double attraction*.

Bergmann's method of determining single elective attractions was as follows. Suppose that the attractive forces of different substances a, b, c, d, etc., for A were to be ascertained. To an aqueous solution of Ad (that is, A saturated with d), he added a little of c in concentrated aqueous solution; if a precipitate formed, he collected that precipitate, washed it, and found by experiments whether it was a new combination, Ac, or the substance d, or a mixture of Ac and d. He then determined "whether the whole of d could be dislodged from its former union by a sufficient quantity of c." He said that it might be necessary to add much more of c "than was necessary to saturate A when uncombined." If the substance c was insoluble,—for example, if it was a metal—Bergmann immersed a plate of c in a solution of Ad, noticed whether precipitation happened, and,

---

[1] "*A Dissertation on Elective Attraction*, by Tobern Bergmann; translated from the Latin by the translator of Spallanzani's *Dissertations*." [London, 1785.] The original memoir appeared in vol. iii of the *Upsala Transactions* [1775].

by putting successive plates of c into Ad, determined whether the whole of d, or only some of it, could be separated. By performing similar experiments with Ad and b, with Ac, Ab, Aa and b, etc., "the order of attractions is discovered." "This however," Bergmann said, "exercises all the patience, and diligence, and accuracy, and knowledge, and experience of the chemist."

Bergmann said that "the only external condition, which either weakens or totally inverts the affinities of bodies subjected to experiments, is the different intensity of heat." The "genuine attractions," or the "free attractions," are those "which take place when bodies are left to themselves."

Bergmann admitted that the order of the attractions, or the affinities, of substances is sometimes apparently altered by solubility or insolubility, by the presence of an excess of one of the substances, and by some other conditions; but he asserted that the real order is constant when the substances react freely in aqueous solutions, and that the order is also constant, although it is not the same as the first order, when the substances react "in the dry way."

Bergmann gave two tables of affinities: one exhibited the attractions "in the moist way," or the "free attractions"; the other showed "those attractions which are effected by the force of heat," or the attractions "in the dry way." For determining attractions in the dry way, Bergmann directed that the reactions of each compound with other substances "should be examined . . . in a crucible, or if possible, in a retort heated to incandescence, that the volatile part may be collected at the same time."

The order of the affinities for any one acid of the various substances mentioned in Bergmann's tables is roughly the same as the order of the affinities of the same substances for any other acid. In his experiments on the precipitation of metals by other metals, Bergmann noticed that "the series of the metals was the same with respect to all the acids." He says: "I was struck with great surprise at the coincidence, considering in how many particulars earths and alkalis differ with regard to them."

I give two columns from Bergmann's tables [1]: one exhibiting the order of the attractions, or affinities, of twenty five substances in solution for vitriolic acid, the other showing the order of the affinities of fifteen substances for gold "in the dry way."

Bergmann said that "to the substances at the heads of the columns those that are placed below bear this relation, that the nearer they stand, the stronger attractions they must be understood to have."

Two columns from Bergmann's *Tables of Affinities*, 1785.

IN THE MOIST WAY.	IN THE DRY WAY.
1. VITRIOLIC ACID	31. GOLD
2. Pure ponderous earth	32. Mercury
3. Pure vegetable alkali	33. Copper
4. Pure solid alkali	34. Silver
5. Lime	35. Lead
6. Pure magnesia	36. Bismuth
7. Pure volatile alkali	37. Tin
8. Pure clay	38. Antimony
9. Calx of zinc	39. Iron
10. Calx of iron	40. Platina
11. Calx of manganese	41. Zinc
12. Calx of cobalt	42. Nickle
13. Calx of nickle	43. Arsenic
14. Calx of lead	44. Cobalt
15. Calx of tin	45. Manganese
16. Calx of copper	46. Saline liver of sulphur
17. Calx of bismuth	
18. Calx of antimony	
19. Calx of arsenic	
20. Calx of mercury	
21. Calx of silver	
22. Calx of gold	
23. Calx of platina	
24. Water	
25. Spirit of wine	
26. Phlogiston	

Most of the attempts which have been made since Bergmann's time to measure affinities have dealt with reactions be-

---

[1] Bergmann represented the substances in his tables by signs. The English edition, from which I have quoted, contains also a translation of these signs into words. Bergmann's tables contain fifty nine columns; the substances at the heads of the columns include many acids, alkalis, earths, and metals, also phlogiston, "matter of heat," etc.

tween substances in solution. The results of attempts to measure the attractions between the particles of elements by determining the relations between the masses of elements which combine, the different degrees of stability of the compounds which are formed, and the quantities of heat produced in the processes of combination have not been particularly encouraging. The curious reader will find much carefully-tabulated data, and many interesting conclusions regarding the attractions between the particles of elements, in a book by Geoffrey Martin, published in 1905,[1] in which, according to the author, there is "the first attempt . . . to systematically collect together data regarding the varying instability of the different compounds which an element produces with other elements, with the object of discovering the law regulating the chemical attraction the elements mutually exert on each other." The author defines chemically analogous compounds to be "compounds in which the attractive forces at play within the molecules are of the same order of magnitude," and he endeavours to establish general relations between the magnitudes of these intramolecular attractive forces.

Bergmann expressed chemical reactions by signs and symbols. I give one example of a Bergmannic chemical equation. This is his representation of "the decomposition of calcareous hepar by the vitriolic acid."
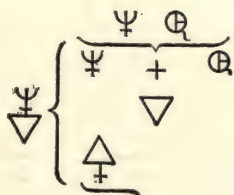
is the sign of calcareous hepar, "with its proximate principles united"; these proximate principles are calcareous earth, and sulphur,

[1] *Researches on the Affinities of the Elements and on the Causes of the Chemical Similarity or Dissimilarity of Elements and Compounds.* [London, J. & A. Churchill, 1905.]

♅ is the sign of vitriolic acid.

△ is the sign of water. Placing the sign for water in the middle intimates "that the three surrounding bodies freely exercise their attractive powers in it."

Separation of the signs of calcareous earth and hepar inside the vertical bracket represents breaking of the combination of these two "proximate principles" by the action of vitriolic acid, which "attracts calcareous earth more strongly than sulphur does." The signs of calcareous earth and vitriolic acid are placed side by side above a complete horizontal bracket—the indication of the formation of a new combination—the point of which is turned downwards to intimate that the new compound (vitriolated calcareous earth or gypsum) is precipitated. The fact that sulphur, which is the other product of the reaction, also precipitates, is indicated by turning downwards the point of the lower horizontal half bracket.

In his memoir on the dissolution of metals in acids,[1] published in 1782, Lavoisier enumerated, very clearly, the forces which he took to be active in the process of dissolving a metal in nitric acid.

"(1) The action of heat which tends to tear apart the molecules of the water and to reduce them to vapour;

(2) The action of the same heat which tends to separate the principles of nitric acid and to convert them into gaseous substances;

(3) The action of the same heat upon the principles which constitute water;

(4) The action of the same heat which decreases the affinity of aggregation of the metal, and tends to break up the parts of it;

(5) The reciprocal action of nitrous gas and oxygen;

(6) The combined action of these two substances in water;

(7) The action of the metal on the oxygen of the acid and on that of the water;

(8) The action of the acid on the metal, or rather on the metallic calx."

"To know the energies of all these forces," Lavoisier said, "to succeed in giving them numerical values, to calculate them, that is the goal which chemistry ought to propose to itself. Chemistry advances slowly, but it is not impossible that it may reach the goal. Meanwhile we are obliged to content ourselves with general considerations. . . . I hope that the reader of this memoir will apprehend the possibility of some day applying exact calculations to chemistry. But, before all, certain data must be obtained which will serve as a foundation, and it is to that subject I mean to devote myself."

---

[1] "Considérations générales sur la Dissolution des Métaux dans les Acides," *Mém. de l' Acad. des Sciences* for 1782, p. 492.

The data which Lavoisier especially mentioned as necessary were the exact composition of water, and the exact composition of each acid the reaction of which was to be investigated.

That portion of the *Encyclopédie Méthodique* which is entitled "Chymie," and was published in 1786, contains a very long dissertation on "Affinité" by Guyton de Morveau, wherein are set forth the views generally held on the subject by chemists in the years preceding the publication of Berthollet's *Essai de Statique Chimique*, which appeared in 1803. When Guyton de Morveau wrote, all chemists, he said, sought for the cause of affinity in the mutual attractions of very minute particles. The relations of the affinities of substances might be examined; the products of the actions of affinities might be investigated for the purpose of classifying the effects of the affinities: these are the two lines on which the study of affinity could be advanced, according to G. de Morveau; the study, he said, had actually advanced for the most part in the direction of classifying the effects of affinities.

Four main classes or kinds of affinity were recognized by G. de Morveau: *affinity of aggregation*, which acts only between molecules of the same kind; *affinity of composition*, which unites different substances so as to produce new homogeneous substances; *disposing affinity*, which "results from a change of the state of composition of one of the substances that it is desired to unite, and produces a combination which would not have been produced without that change"; *affinity by joint action*, which is the same as *double affinity*, and comes into play when four, or more than four substances react chemically.

Some chemists, G. de Morveau said, were trying to reduce the phenomena of affinity to a general system,

"in order to deduce therefrom a certain number of principles or constant laws, which, always present in the mind, are able habitually to recall those fundamental truths that throw the light of analogy on the most obscure facts. . . . I will not take account of these generalizations except of those which are the most certain; the number of them is limited enough, and perhaps they do not all deserve to be called laws of affinity."

The "laws of affinity" recognized by G. de Morveau were these.

I. *Corpora non agunt nisi fluida.*

II. Affinity is manifested only between the smallest integrant molecules of substances.

III. Excess of one or other of two substances modifies their affinities.

IV. That "affinity of composition" may be effective, it must exceed "affinity of aggregation."

V. The product of the action of "affinity of composition" is a distinct substance, with properties of its own, unlike those of the two or more substances which have united to produce it.

VI. There is a condition of temperature which makes the action of the affinities of substances slow or rapid, of no account or efficacious.

The principal methods which had been proposed for measuring the strengths of affinities are then criticised by Guyton de Morveau. He takes Kirwan's method to be, on the whole, the most satisfactory.

Kirwan[1] found the quantities of "real acid" in aqueous solutions of certain mineral acids, by measuring the specific gravities of the solutions, and then determined the weights of various bases which saturated these acids, that is, formed neutral salts with them. He concluded that the weights of bases required to saturate a determinate weight of an acid are directly as the affinities of the acid for the bases.

The following table is given by Guyton de Morveau.

QUANTITIES OF BASES WHICH 100 GRAINS OF EACH OF THE MINERAL ACIDS
REQUIRE FOR THEIR SATURATION.

	Potash.	Soda.	Lime.	Ammonia.	Magnesia.	Alumina.
Vitriolic acid	215	165	110	90	80	75
Nitric acid	215	165	96	87	75	65
Muriatic acid	215	158	89	79	71	55

From these data, G. de Morveau concluded, provisionally, that the affinity of vitriolic acid for potash (that is, the force

---

[1] *Phil. Trans.* for 1781, p. 9.

wherewith they unite or tend to unite) is to the affinity of the same acid for lime as 215 is to 110.

The difficulties attending the application of Kirwan's method for determining the affinities of acids and bases were considered in detail by G. de Morveau. One great difficulty was the fact that the compositions of the same neutral salts were represented by different numbers by Bergmann, Wenzel, and Kirwan. Guyton de Morveau concluded that no certain and generally applicable method for determining affinities was available when he wrote; all that could be done was to take the results of the precipitation of various substances by one another, and to apply these tentatively to more complex cases. He came to much the same general conclusions as those arrived at by Bergmann; the order of affinities is constant, but is apparently modified by temperature, by double affinities, by solubility or insolubility, and by the presence of excess of one or other of the constituents of a salt.

I append one of Guyton de Morveau's tables.

TABLE OF THE NUMERICAL EXPRESSIONS OF THE AFFINITIES OF FIVE ACIDS AND SEVEN BASES, ACCORDING TO THE CONSTANT RELATIONS INDICATED BY THE BEST-KNOWN OBSERVATIONS.

	Acide vitriolique.	Acide nitreux.	Acide muriatique.	Acide acéteux.	Acide mephitique.
Barote	65	62	36	29	14
Potasse........	62	58	32	26	9
Soude.........	58	50	28	25	8
Chaux.........	54	44	20	19	12
Ammoniac......	46	38	14	20	4
Magnésie	50	40	16	17	6
Alumine........	40	36	10	15	2

In the year 1801, Berthollet published a very important memoir on the laws of affinity.[1] Two years later, the same naturalist produced his celebrated *Essai de Statique Chimique*, wherein he amplified and illustrated in great detail the conclusions which he had arrived at in his memoir. Berthollet

[1] "Recherches sur les lois de l'affinité, par le citoyen Berthollet," *Mém. de l'Institut National des Sciences et Arts. Sciences Mathématiques et Physiques.* Tome troisième. Paris, Prairial An IX., pp. 1, 207, 229. A note appended to the memoir says: "La lecture de ce mémoire a été commencé dans les scéances de l'Institut du Caire en messidor an 7." [1799.]

opposed the doctrine, which most chemists thought Bergmann had firmly established, that substances can be arranged in the order of their affinities for a standard substance, and each one will completely displace from their combinations with the standard substance all the others whose affinities for that substance are weaker than its own.

The picture which Berthollet formed in his mind of chemical actions was this:

"Chemical action is reciprocal; its effect is the result of a mutual tendency to combination. Strictly speaking, we cannot say that a liquid acts on a solid rather than that the solid acts on the liquid. For the purpose of convenient expression, however, we assign all the action to one of the two substances when we wish to examine the effects of that action rather than the action itself." [1]

Berthollet emphasized the resemblances between chemical changes and processes of dissolution. He held that there is no difference of kind, but only differences of degree between the two occurrences. The striking features of a process of dissolution, Berthollet said, are the disappearance of a solid and the uniformity of the liquid which is formed. The combination of the solvent with the dissolved substance is generally so feeble that the properties of both are discernible in the solution. But, Berthollet remarked, the differences between the constituents of a chemical combination and those of the compound are generally so marked that attention is arrested by them, the essential similarity between the process of dissolution and that of the formation of a chemical compound is overlooked, and the laws which express the facts of the first kind of change are supposed to be inapplicable to the second. Processes of dissolution are gradual; Berthollet taught that chemical actions proceed continuously, and are conditioned chiefly by the affinities and the quantities of the reacting substances. The combinations of two substances which react chemically form a series, as the combinations of a solvent with the substance dissolved in it form a series. In many chemical reactions, Berthollet said, there are points whereat some force, and more particularly the force of cohesion, overcomes the force of affinity; when one of these

---

[1] *Essai*, pp. 36, 37.

points is reached, the constituents of the product formed by the action of the affinities are combined in definite and fixed proportions, and chemical action stops. But, according to Berthollet, a series of combinations is formed before the points of maximum stability are reached, as a series of combinations is formed before saturation is attained in a process of dissolution. That I may make Berthollet's conceptions clear to the reader, I quote what he says in the fourth paragraph of the first section of his *Recherches*:

"The whole of Bergmann's doctrine is founded on the supposition that elective affinity is a constant force, of such a nature that a substance which causes the separation of another from its combination cannot itself be displaced from the new combination by that substance which it has eliminated. . . . I propose to prove in this memoir that elective affinities do not act as absolute forces by which one substance would be replaced by another from its combination; but that, in all the compoundings and decompoundings which are caused by elective affinities, there is a partition of the basis of the combination between the substances whose actions are opposed to one another (*il se fait un partage de l'objet de la combinaison entre les substances dont l'action est opposée*), and that the proportions of this partition are determined not only by the energy of the affinity of these substances, but also by the quantity with which they react, so that quantity is able to do duty for the force of affinity in producing an equal degree of saturation. If I prove that the quantity of a substance can take the place of the force of its affinity, it follows that the action of the substance is proportional to the quantity of it that is required to produce a determinate degree of saturation. I denote that quantity by the term *mass*, and I take it to be the measure of the capacity of saturation of different substances. When, therefore, I am comparing the affinities of substances, I will direct my attention to the ponderable quantities of them, which must be taken as equal in that comparison; but when I am comparing their action, which is composed of their affinity and their proportion, I must consider their *mass*."

Bergmann had taught that when a substance A reacts with a compound BC, the substance B is replaced by A, and the new compound AC is produced. Berthollet said that, in such a case,

"I must prove that in opposing A to BC, the combination AC will not be formed unless there be the concurrence of another force; but that C will divide itself between A and B in proportion to their affinity and their quantity, —in other words, in proportion to their mass."

It is evident that Berthollet did not give to the word *mass* the meaning which is given to it to-day; he used the term as a

convenient expression for the product of the quantity and the affinity of a substance.

Berthollet proposed to prove his generalizations by experiments on reactions between acids and alkalis, using the term *alkali* to include the earths; then to show that reactions between other compounds confirmed his principle, and indicated the range of its application; then to examine the circumstances which modified the law that chemical action between unlike substances is proportional to their affinities and their quantities, in other words, to consider

"the quantities of substances which favour or lessen their chemical actions, and cause variations in the proportions of the combinations which they are able to form." Finally, he said, "I shall attempt to settle the foundation on which the general and the special theories of chemical phenomena ought to be based." [1]

There can be no doubt that Berthollet firmly established the general principle that

"every substance which tends to enter into combination acts in proportion to its affinity and its quantity." [2]

As he recognized that the chemical action of a substance is conditioned by the state of its parts, that is, by any circumstance which alters the affinities of the parts—for instance, condensation, expansion, or chemical actions which have preceded the action under consideration—Berthollet was obliged to examine the modifying effects of various circumstances on special cases of chemical change. In his *Recherches*, speaking of the interactions of two, of three, or of several substances, he says:

"In all cases where liquids are concerned there is mutual saturation; hence a simple combination is formed, provided that all the forces find themselves counterbalanced, and neither precipitation nor disengagement of an aeriform substance happens. But, inasmuch as the action is divided if there be an opposition of forces and a difference of saturation, in that case certain substances are retained in the new combination more feebly than before the mixture; these substances are in a position to yield to the force of cohesion, or of elasticity, or of other affinities, which they were formerly able to resist." [3]

[1] *Recherches*, par. 7, Article I.
[2] *Essai*, p. 2.
[3] *Recherches*, par. 7 of *Résumé*.

Berthollet's position is perhaps made clearer by reading his remarks on the reactions between two acids and one alkali.

"When two acids act on one alkali, an equilibrium of saturation is attained, which is the product of the quantity of each of the two acids and of the relative capacity of saturation. But when one combination forms and is precipitated, an equilibrium is established between two compounds which exert opposing forces. One of these is the insoluble combination, and the other is the combination which remains liquid in presence of an excess of acid. The acid exhausts its solvent action on the insoluble substance, with a result which is dependent on the insolubility as compared with the energy of the acid. Now, as the actions of acids are proportional to their quantities, it is possible, by increasing the quantity of the acid which acts in opposition to the insolubility, to decrease the insolubility of the precipitate, or even to cause the precipitate to disappear, unless the force of cohesion should be great enough to prevent its yielding to the other force which tends to overcome it." [1]

How did Berthollet propose to measure affinities? In his *Essai*, Berthollet says: [2]

"I consider that each of the acids which compete for an alkaline base acts in proportion to its mass [that is, quantity multiplied by affinity]. In order to determine the masses, I compare the capacities of saturation, whether of all the acids with one base, or of all the bases with one acid."

This sentence indicates Berthollet's method for determining the relative affinities of two acids. The method is described more definitely in Article X of his *Recherches*.

"To determine the elective affinity of two substances for a third, in accordance with the idea which we ought now to have formed of affinity, is to discover the proportion wherein that third substance must divide its action between the first two, and the degree of saturation which each of the latter must attain when the force of one is opposed to that of the other. The relative affinities will be proportional to the degrees of saturation attained, referred to the quantities which have reacted; so that, if these quantities are equal, the comparative degree of saturation should be the measure of the relative affinities."

Berthollet was careful to explain what he meant by *saturation*.

"When I speak of the saturation of a substance, I do not mean that absolute saturation whereat all mutual action would cease. I mean a degree

of saturation which is easily discovered, and is common to all combinations; I mean the saturation that is attained when the properties of neither of the constituent parts overpower those of the other." [1]

Berthollet insisted that throughout every series of experiments wherein comparisons of affinities are made, the same proportion must be maintained between the quantities of the reacting substances. For example: suppose that 100 parts of potash are saturated by 100 parts of sulphuric acid, and that it is desired to determine the relative affinities of potash and soda towards that acid; 100 parts of the acid must be allowed to react with a mixture of 100 parts of potash and 100 parts of soda. If it is found that the acid has taken 60 parts of the potash and 40 parts of the soda, the conclusion is drawn that the relative affinities of the two bases for sulphuric acid are in the ratio of 60 to 40. In this case, the 40 parts of potash which have not combined with acid continue to react, according to Berthollet, and influence the partition of the acid. If 80 parts of potash and 80 parts of soda were used, 20 parts of potash and a different quantity of soda would remain uncombined; so that the forces exerted by those uncombined portions of the two bases would not be the same as in the former experiment, and the two saturations would not be in the proportion of 60 to 40.

How is one to discover the quantity of each compound which is formed when two substances in solution react with a third also in solution; when two alkalis, for example, react with an acid? The separation of the compounds from the liquid wherein they are dissolved cannot be effected, Berthollet points out, without introducing the action of extraneous forces—elasticity, crystallization, precipitation—and the results are due, not solely to the action of affinity, but to the concurrent actions of several forces. Berthollet regarded the difficulties in this part of the problem to be insurmountable.[2] These difficulties were overcome about sixty years after the publication of Berthollet's *Essai*.

It might be supposed, Berthollet said, that measurements of the capacities of saturation of different acids by a base, or of

---

[1] *Recherches*, Art. X, par. 2.
[2] *Recherches*, par. 4 of *Résumé*.

different bases by an acid, would establish the relative affinities of these compounds; for would not the affinities be inversely proportional to the quantities required to produce the same degree of saturation? That conclusion would be erroneous, Berthollet said,[1]

"because, when two substances are allowed to react with a third, new forces are brought into play which not only cause other results, but even change the constitution of the substances concerned."

Suppose that carbonic acid is neutralized by potash, the acid exerts a force equal to that exerted by sulphuric acid in producing the same effect; but if sulphuric acid is added to the combination of carbonic acid and potash, the whole of the carbonic acid is disengaged, and even if it is retained by a sufficient quantity of water, "it will not have the same constitution [as before], it will not be the same substance so far as chemical action is concerned."

"The comparison of capacities of saturation may lead to important considerations, but cannot be applied to the determination of elective affinities."

Berthollet regarded chemical action to be dependent on the quantities and the affinities of the reacting substances, and he asserted that the quantities of the substances in the sphere of activity are conditioned by the action of cohesion, of insolubility, and of elasticity; he also traced a very close similarity between chemical actions and processes of dissolution. One of the conclusions to which these general conceptions led him was that fixity of composition is not the rule, but is the exception among chemical compounds. That conclusion we know to be erroneous. Proust combated Berthollet's conclusion regarding fixity of composition. By following, step by step, the experimental evidence which led Berthollet to state that the compositions of only a few compounds are always the same, and proving the existence of many errors in Berthollet's work,

---

[1] *Recherches*, par 5 of Art. X. By *constitution* of a substance, Berthollet meant what we now call its *physical state*.

Proust established the fact that the constituents of at least very many compounds are combined in fixed proportions.[1]

Berthollet concludes the first section of his *Recherches* thus:

"The considerations which I have presented concerning the modifications of chemical action do not prevent us from using the term affinity of a body to mean the whole chemical power which it exerts in determinate circumstances, whether it be by virtue of its actual constitution, by virtue of its proportion, or even by the joint action of other affinities. But what must be avoided is to consider that power to be a constant force which produces compositions and decompositions; to conclude, from what it is, what it ought to be under other conditions which may give to it a very different degree of force; to neglect all the modifications which it experiences from the time of its initial action until equilibrium is attained."

Berthollet's work emphasized and amplified the views which had been expressed by Wenzel twenty-four years before the appearance of Berthollet's *Recherches*. Wenzel regarded chemical processes in solutions as the results of the actions and reactions of opposing forces which are modified by various conditions.[2] Berthollet made this conception more comprehensive and more definite.

To accept Berthollet's conclusion, that each substance which takes part in a chemical change reacts in proportion to its affinity and the quantity of it in the sphere of activity, would be to pronounce the elaborate *tables of affinity*, which were the outcome of so many years of laborious experimenting, to be far from a final solution of the fundamental problem of affinity. It was impossible for chemists to accept Berthollet's generalization without protest.

The first part of Dalton's *New System of Chemical Philosophy* was published (in 1808) five years after the appearance of Berthollet's *Essai*. Many chemists thought that Berthollet's views on chemical action were contradicted by the Daltonian theory. For example, in the fifth edition of his *System of Chemistry*, published in 1817, Thomson said:

"The atomic theory seems to me to present an insuperable objection to the opinion advocated by Berthollet that *mass* produces an effect upon chemical combinations and decompositions."

[1] *Journal de Physique;* translations in *Nicholson's Journal* for 1802, 1806, 1807, 1810. For a few details about Proust's work see Chapter III, pp. 75, 76.
[2] Compare p. 383.

We now know that there is no difficulty in reconciling Berthollet's generalization with the atomic theory of Dalton; we also know that Berthollet's attempt to prove the variability of composition of most compounds failed because it was met by the "insuperable objection" of facts.

Berthollet started by taking a wide survey of certain classes of chemical facts, and tracing broad analogies between these facts and others which were generally supposed to belong to the domain of physics. That survey, and these analogies, led him to a very comprehensive generalization, which he attempted to apply to particular classes of chemical reactions. The experimental difficulties in the way of these applications could not be overcome by the machinery which was available in his day. One of his particular applications has been proved to be correct; another has been proved to be incorrect.

Unfortunately Berthollet forgot, what Dalton so vividly realized, that "brevity is the soul of wit," and expanded his conceptions in a very lengthy and not particularly interesting treatise.

It is instructive to compare the method of Berthollet with those of two other great chemists. Berthollet took a very comprehensive, but somewhat vague, general view of a large tract of chemical country. Berzelius made a sharply-defined and very accurate study of a series of chemical questions, all bound together by one penetrating idea. Lavoisier conducted an incisive examination of the essential features of a few special cases of chemical change, and arrived at conclusions which have been found to cover a large part of the field of chemical inquiry.

Between the time of the publication of Berthollet's *Essai* and the year 1867, many important contributions were made towards elucidating the relations between the amounts, and also between the rates of chemical changes, and the affinities and the quantities of the interacting substances. These contributions dealt with special cases of reactions: in some of them conclusions were drawn which were found to be capable of general application; in some were introduced new methods of determining the amount of chemical change which occurred in systems composed entirely of liquids or of substances in solution.

I ask the reader to pass over the sixty five years or so which separate the publication of Berthollet's *Essai* from the appearance of Guldberg and Waage's *Studies in chemical affinity*.[1]

Considering chemical changes of the types $AB + C = AC + B$, and $AB + CD = AC + BD$, Guldberg and Waage said:

"The formation of AC is brought about chiefly by the attractions between A and C; but there will also be certain attractions between the other substances, and the *force* which brings about the formation of AC is the resultant of all these attractions. That force may be regarded as constant at a determinate temperature, and we represent its magnitude by K, which we call the *coefficient of affinity* for that reaction. Similarly, the force which produces the new substances in the *double substitution* $AB + CD = AC + BD$ is a function of all the attractions between the substances A, B, C, D, AB, AC, CD, and BD, and that resultant force, K, is the *coefficient of affinity* for the reaction."

For the study of the relations between coefficients of affinity, Guldberg and Waage chose changes of composition wherein equilibrium is attained by the balancing of reactions, changes which are represented by the general expression $A + A \rightleftarrows A' + B'$, changes wherein equal numbers of equivalents of $A' + B'$ and of $A + B$ are formed in unit time. They say:

"The force which brings about the formation of A' and B' increases *in proportion to the coefficient of affinity for the reaction* $A + B = A' + B'$; but it depends also on the masses of A and B. We conclude, from our experiments, that *the force is proportional to the product of the active masses of the two substances* A and B."

In the memoir of 1867, Guldberg and Waage defined the *active mass* of a substance to be the quantity of it in "the sphere of attraction" or "the sphere of action," that is, in "a sphere traced with a radius equal to the distance outside of which the influence of chemical attraction is insensible." As they could not determine the absolute sizes of the spheres of action, they chose an arbitrary volume; if 1 c.c. were chosen, the active mass of a substance would be the quantity of it in 1 c.c. of the solution under examination.

---

[1] *Études sur les Affinités Chimiques*, par C. M. Guldberg et P. Waage [Christiania, 1867]. A second memoir, "Ueber die chemische Affinität," by the same authors, appeared in 1879 in *J. prakt. Chem.* [2], **19**, 69. No. 104 of Ostwald's *Klassiker der exakten Wissenschaften* consists of these two memoirs (in German), and two short communications made in the year 1864 by the same authors.

Guldberg and Waage's application of their statement that the force which brings about the formation of A′ and B′, in the reaction $A + B \rightleftarrows A' + B'$, is proportional to the active masses of A and B, proceeded on the following lines. They expressed the force as $k \cdot p \cdot q$, where k is the coefficient of affinity and p and q are the active masses of A and B; and, in order to simplify the problem, they ignored all other forces which might tend to accelerate or to retard the formation of A′ and B′. Similarly, they expressed the force which produced A and B from A′ and B′ as $k' \cdot p' \cdot q'$, where p' and q' are the active masses of A′ and B′. When the two forces are in equilibrium, the active masses remain unchanged, and

$$k \cdot p \cdot q = k' \cdot p' \cdot q'.$$

Guldberg and Waage say (*Etudes*, p. 7):

"Let us express by P, Q, P′, and Q′, the absolute quantities of the four substances A, B, A′, and B′, before the reaction begins, and let x be the number of atoms of A and B which are transformed into A′ and B′; moreover, let us suppose that the total volume is constant during the reaction and is equal to V; we shall have

$$p = \frac{P - x}{V}, \quad q = \frac{Q - x}{V}, \quad p' = \frac{P' + x}{V}, \quad q' = \frac{Q' + x}{V}.$$

By substituting these values in the first equation, and multiplying by V^2 we obtain

$$(P - x)(Q - x) = \frac{k'}{k}(P' + x)(Q' + x).$$

It is easy to find the value of x by the help of this equation."

When x has been found for any special case, $\frac{k'}{k}$ can be calculated; x can then be determined for any initial value of P, Q, P′, and Q′, and hence the distribution of the substances can be found when equilibrium is attained in that system.

It is evident from their experimental results that, in 1867, Guldberg and Waage measured the quantities P, Q, P′, Q′, and x in numbers of equivalents (that is, quantities by weight divided by equivalent weights). In their later memoir (1879)

they gave a presentation of reactions of the type $A + B \rightleftarrows A' + B'$ in terms of the molecular and atomic theory; that presentation led them to an equation wherein the active masses of the reacting molecules were raised to the power which expressed the number of these molecules. That equation will be described on page 403. We shall see in the next chapter that the general theory of chemical equilibrium includes the conception of active mass.

In their *Études*, Guldberg and Waage developed equations for expressing the conditions of equilibrium in more complex systems than those which initially contained only two substances. They supposed that the forces between those substances which are not represented by the ordinary chemical equations as taking a direct part in the changes of composition in a system, are proportional to the active masses of these substances and to certain coefficients which they called *coefficients of action*. They said that these coefficients of action are generally less than the coefficient of affinity, and that the total force is, therefore, generally positive; but, they remarked, the coefficients of action may balance the coefficient of affinity, and no action may happen in systems wherein there would be positive action between the principal components (A and B) were the other foreign substances absent.

In the eighth section of their *Études*, Guldberg and Waage consider the determination of chemical affinity from measurements of the velocities of reactions.

"When two substances A and B are changed into two new substances A' and B', we call the quantity of $A' + B'$ which is formed in unit time the *velocity* of the reaction, and we establish the law that *the velocity is proportional to the total force of A and B*. Assuming that the new substances A' and B' do not react on one another, we shall have

$$v = \phi \mathrm{T},$$

where v is the velocity, T is the total force, and ϕ is a coefficient which we call the *coefficient of velocity*. . . . Representing by x the quantities of A' and B' which are produced in the time t, it will be possible to express the total force, T, as a function of x, and, noting that $v = \dfrac{dx}{dt}$, it will be possible . . . to determine x as a function of t. The equation which is found between x

and t will serve to determine the *coefficients of affinity* and the *coefficients of action*."

Guldberg and Waage developed the above equation, and applied it to the results of many measurements of the velocities of chemical changes. In the memoir of 1879, they give the following presentations of the velocity of the reaction $A + B = A' + B'$.

"If p and q denote the number of molecules of A and B in unit volume, the frequency of the encounters of the molecules of A and B is represented by pq. If every meeting of the different kinds of molecules were equally favourable to the formation of new substances, the rate whereat the chemical change proceeds, or, in other words, the quantity which is transformed in unit time, may be put as equal to ϕpq, where the coefficient of velocity, ϕ, is to be considered as dependent on the temperature. . . . Of the p molecules of A which are present in unit volume, only a fraction, a, will generally be in a condition such that their encounter with molecules of B will be the cause of substitution. Similarly, of the q molecules of B which are present in unit volume, only a fraction, b, are so conditioned that their encounter with molecules of A is the occasion of a process of substitution. Hence, in unit volume, there are ap molecules of the substance A, and bq molecules of the substance B which can be transformed into new substances when they encounter one another. Therefore the frequency of the encounter of decomposable molecules will be represented by the product $ap \cdot bq$, and the rate at which the formation of the new substance proceeds is expressed by

$$\phi apbq;$$

or, if ϕab is put as $= k$, the expression becomes

$$kpq.$$

This way of looking at the question is capable of greater extension; it may be applied to every reaction whatever be the number of substances concerned therein. For example, if it is necessary for the formation of new compounds that three substances A, B, and C, should encounter one another, and if the numbers of molecules of these substances which are contained in unit volume are severally expressed by $p, q,$ and r, and, finally, if the specific coefficients of the substances are denoted by $a, b,$ and c, the expression of velocity is

$$\phi \cdot apbqcr = kpqr$$

when the product of the coefficients is expressed by k.

But if there be, for example, an addition-compound $\alpha A + \beta B + \gamma C$, which is composed of α molecules of A, β molecules of B, and γ molecules of C, the velocity is expressed thus

$$\phi ap \; ap \ldots bqbq \ldots crcr \ldots$$
$$= \phi a^{\alpha} \; p^{\alpha} \; b^{\beta} \; q^{\beta} \; c^{\gamma} \; r^{\gamma}$$
$$= k p^{\alpha} \; q^{\beta} \; r^{\gamma},$$

where k signifies the product of all the coefficients."

All that need be done in order to find the conditions of equilibrium is "to put the velocities of the two opposing reactions as equal." "The absolute velocity of the chemical reaction is, evidently, equal to the difference between the velocities of the two opposing reactions."

On the assumption that secondary reactions may be ignored, Guldberg and Waage developed their hypothesis of mass-action, and applied it to various systems of chemically reacting substances. The classes of reactions for which they found the appropriate equations were these: systems of four soluble substances; systems composed of two soluble and two insoluble substances; systems composed of three soluble substances and one insoluble substance; systems composed of an arbitrary number of soluble substances; systems composed of soluble substances and gaseous substances which are absorbed by the solution; systems composed of gaseous substances produced by the dissolution of a solid substance; and, finally, systems composed of gaseous substances. Taking several special cases in each of these classes of reactions, Guldberg and Waage showed that the amount of chemical change which was determined experimentally agreed very well with the amount which was calculated by the use of their equations, all of which were developments of the fundamental expression, $kpq = k'p'q'$.'

Towards the close of their *Études* (1867) the Norwegian naturalists say:

"These are the series of experiments to which we have applied calculations. We think they are sufficient to establish the probability of our theory; the divergences between the observed and the calculated results are due to something which we have neglected, the presence of salts formed during the reactions, and, in many cases, certain coefficients of action which are probably not sufficiently small to be neglected. . . . In beginning our studies in 1861, we thought it might be possible to find numerical values for the magnitudes of chemical forces. We also thought that we might find for each element and for each chemical compound certain numbers which would express their relative affinities, as atomic weights express their relative weights

. . . Although we have not solved the problem of chemical affinities, we think that we have indicated *a general theory of some chemical reactions*, namely, those wherein *a state of equilibrium is produced* between opposing forces. . . . The aim of our memoir has been to demonstrate, first, that *our theory explains chemical phenomena in general, and, secondly, that the formulæ which are based on the theory accord sufficiently well with the numerical results of experiments.* . . . All our wishes would be accomplished if we could succeed in drawing the serious attention of chemists, by means of this work, to a branch of chemistry which has undoubtedly been too much neglected since the beginning of this century."

The hopes of Guldberg and Waage have certainly been realized.

The conceptions of balanced actions and the conditioning effects of various circumstances on chemical affinity, which were adumbrated by Wenzel in 1777, and were made more exact and more directly applicable to definite reactions by Berthollet in the first year of the nineteenth century, were put into a form which made it possible to test their usefulness by the results of quantitative experiments by Guldberg and Waage sixty six years after the appearance of Berthollet's memoir. Both Berthollet and Guldberg and Waage regarded those reactions which proceed in one direction only, and were usually thought of as completed processes, to be limiting cases of the general reaction which is composed of a direct and a reverse change, the general reaction which has the form

$$A + B + C + \ldots \rightleftarrows A' + B' + C' + \ldots$$
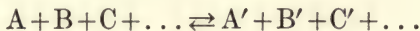
Berthollet proposed to measure the affinities of acids by determining the partition of a base between two acids in aqueous solutions; Guldberg and Waage followed the same method; but whereas Berthollet allowed a base to react with equal weights of two acids, Guldberg and Waage used masses of the three compounds which were proportional to their equivalent weights. Guldberg and Waage made the correction which was required in order to arrive at accurate determinations of the relative affinities of compounds; moreover, they included in the theory of chemical changes those facts of equivalence and of fixity of reacting masses which seemed to many of those who criticised the work of Berthollet to be irreconcilably opposed to the general theorem

which Berthollet enunciated, that "every substance which tends to enter into combination acts in proportion to its affinity and its quantity."

In 1877 van't Hoff [1] showed how the equation of equilibrium of Guldberg and Waage may be obtained by considering the velocities of reactions without introducing the somewhat vague idea of chemical force.

The law of equilibrium of homogeneous systems, that is, systems in which there is not at any time a surface of separation, is generally stated in the following form. Let A, B, C, . . . react to produce D, E, F, . . . and D, E, F, . . . react to produce A, B, C, . . .; let the concentrations of these substances—that is, the quantity of each divided by the total volume—be represented by $a_1, a_2, a_3 \ldots b_1, b_2, b_3 \ldots$; and let $m_1, m_2, m_3 \ldots n_1, n_2, n_3 \ldots$ be the number of molecules of A, B, C . . . D, E, F . . . which take part in the reaction; then equilibrium is attained when

$$a_1{}^{m_1}a_2{}^{m_2}a_3{}^{m_3} \ldots = kb_1{}^{n_1}b_2{}^{n_2}b_3{}^{n_3} \ldots ,$$

where k is a coefficient which depends on the nature of the substances and the temperature. When the law of equilibrium of homogeneous systems is applied to the relations between the rate of a chemical change and the quantities of the changing substances, it asserts that the rate of action is equal to the product of the molecular concentrations multiplied by a constant which is dependent on the nature of the substances and the temperature. (A fuller treatment of the history of chemical equilibrium will be found in Chapter XV.)

Some of the applications of the fundamental law of mass-action to chemical systems will be glanced at in the chapter on Chemical Equilibrium (Chapter XV.).

Berthollet recognized that the affinities of compounds could not be determined until methods had been elaborated for measuring the partition of one substance between others when all react freely in solution; he regarded the ordinary methods of analysis to be incapable of application to this problem, and he did not discover any way of solving the problem.

---

[1] *Berichte*, **10**, 669 [1877].

Steinheil [1] showed, in 1843, that the arrangement of the constituents of a solution could be calculated from measurements of some one or other of the physical properties of the solution. Biot [2] had shown, in the thirties of the nineteenth century, that the changes in the rotation of the plane of polarization of light by aqueous solutions of tartaric acid were not proportional to the quantities of the acid in solution, and had concluded that chemical action occurred between the acid and the solvent; moreover, he had shown how to determine the amount of chemical change by measuring the variation of rotation. In 1850, Wilhelmy used measurements of the change of rotatory power in solutions of cane sugar, mixed with determinate quantities of different acids, to determine the rate of production of glucose. [3] In the fifties of last century, J. H. Gladstone [4] used the colours of solutions produced by mixing various salts to determine the distributions of the constituents of these solutions. In 1869, J. Thomsen [5] made approximate determinations of the partition of a base between two acids, in dilute solution, by measuring the thermal values of the changes and of different parts of them. In 1876, Ostwald [6] began a series of measurements of the changes in the volumes, and also in certain optical properties of solutions of acids and bases when these were mixed, and deduced from his results the distribution of the reacting substances.

By these, and by other similar methods, data were obtained regarding the distribution of the compounds in various systems of homogeneous substances, when these systems had attained equilibrium by the actions and reactions of their constituents.

The law of mass-action, which was stated by Berthollet and was quantitatively applied by Guldberg and Waage, enabled determinations to be made of the ration $\frac{k'}{k}$, that is, of the relative affinities of two substances for a third wherewith both interact,

[1] Annal. Chem. Pharm., **48**, 153 [1843].

[2] Compt. rendus for 1835.

[3] Pogg. Annal., **81**, 413, 499 [1850].

[4] Phil. Trans. for 1855, 179.

[5] Pogg. Annal., **138**, 65 [1869]. Thomsen's method will be sketched in Chapter XVI.

[6] J. prakt. Chem. (2), **16**, 385 [1877]; **18**, 328 [1878].

and more particularly of the relative affinities of two acids for the same base, and of two bases for the same acid, when equivalent quantities of the three compounds interact in dilute solution. The ratio of the distribution of the base between the acids is the ratio of the affinities of these acids for that base; the ratio of the distribution of the acid between the bases is the ratio of the affinities of the bases for that acid.

In 1877, Ostwald demonstrated that the relative affinities of acids are independent of the composition of the base, and the relative affinities of bases are not altered by changing the acid wherewith they interact.[1]   This result was analyzed by Ostwald, who showed that it led to the following conclusion.[2]

"The affinity between acids and bases is . . . the product of specific affinity-coefficients. All reactions due to acids and bases, as such, must . . . be proportional among themselves. From this it follows that processes which, taken by themselves, have nothing to do with the formation of salts, may be employed for finding numerical values for the affinities which come into play during the formation of salts, provided that the reactions in question have been accomplished by the acids and the bases only. Determinations of the specific affinity-coefficients of acids and of bases are thus of the greatest importance."

By measuring the effects of determinate quantities of different acids on the rate of change into ammonium acetate of a dilute aqueous solution of acetamide,[3] and by determining the rate of change of methyl acetate into methylic alcohol and acetic acid, in the presence of different acids,[4] Ostwald obtained values for the affinities of many acids referred to that of hydrochloric acid taken as unity.   As the order of the magnitudes of the affinities determined by using these two reactions (which are very different from those wherein salts are formed by the interactions of acids and bases) was found to be the same as the order of the magnitudes determined by measuring the partition of a base between two acids, the reasoning was justified which led Ostwald to the conclusion that

---

[1] *J. prakt. Chem.* (2), **16**, 385 [1877].   Compare the quotation from Bergmann, p. 385.

[2] The quotation in the text is from the article "Affinity," by Ostwald, in vol. i (pp. 67–87) of *Watts' Dictionary of Chemistry* [new edition, 1888].

[3] *J. prakt. Chem.* (2), **27**, 1 [1883].

[4] *Ibid.*, **28**, 449 [1883].

"the numerical values of all reactions exhibited by acids, as such, depend on that one property which till now has been somewhat vaguely termed the *strength* of the acids." [1]

The measurements of the rate of change of cane sugar to glucose, in presence of different acids, which he made in 1884 and 1885, gave Ostwald [2] a new series of values for the acids whose affinities he had determined by other methods. By whatever methods the affirnities were determined, the order of their values was the same. Ostwald showed that the variations in the actual values obtained by different methods were due to secondary reactions which were overlooked in the calculations, and that these secondary reactions had a greater influence in some of the processes which he employed than in others.

The general conclusions to be drawn from the work of Ostwald which has been sketched were, that each acid, and also each base, has an affinity-coefficient which quantitatively determines all its specific reactions, and, the relative values of these coefficients can be determined with approximate accuracy by various methods, some of which may be called physical, and others, chemical methods.

In Chapter XII (pp. 322 to 333) I sketched the history of the demonstration that the readiness wherewith electricity is transported by the ions of electrolytes is proportional to the rates of the chemical reactions which are dependent on these electrolytes, and that there is no proportionality between the electrolytic conductivities of compounds and the affinities which the Berzelian doctrine of electrodualism attributed to their ions. In the same chapter (p. 334) I quoted Helmholtz's statement of Faraday's law:

"The same quantity of electricity passing through an electrolyte either sets free, or transfers to other combinations, always the same number of units of affinity at both electrodes."

I warned the reader that by *the same number of units of affinity* Helmholtz meant the same number of atomic valencies;

[1] Ostwald, *Watts' Dictionary of Chemistry*, vol. i, p. 80.
[2] *J. prakt. Chem.* (2), **29**, 385 [1884]; (2) **31**, 307 [1885].

and I drew attention to the very unfortunate use, by chemists, of the term *affinity* to express two very different conceptions.

The investigations of Faraday, which culminated in the demonstration that equivalent quantities of substances have equal quantities of electricity associated with them, disproved, once and for all, the Berzelian hypothesis that a greater quantity of electricity is needed to separate a compound of a very positive with a very negative element, or radical, than is required to separate a compound of a less positive with a less negative element, or radical. But, at the same time, Faraday's researches very greatly strengthened that part of the Berzelian doctrine which asserted the existence of a close connexion between electrical and chemical forces.

As the existence of a close connexion between the electrical conductivities and the chemical reactions of acids in aqueous solution had been established, it followed, from Ostwald's measurements of the relative affinities of acids, that the conductivities are very probably proportional to the velocities of the reactions produced by acids. In 1884, Ostwald[1] determined the electrolytic conductivities of thirty four acids, and showed that the values obtained agreed very closely with the rates of inversion of cane sugar, and with the rates of change of methyl acetate, in the presence of the same acids. Hence, it seemed that the relative affinities of acids and of bases might be determined by measuring the electrical conductivities of their aqueous solutions. We must examine in some detail the history of the electrochemical method of determining the relative affinities of acids.

In 1885, Ostwald began an extensive series of measurements of the molecular conductivities of acids in aqueous solution. The *molecular conductivity* of an electrolyte was defined by Ostwald[2] to be "that quantity of electricity which passes in one second between two electrodes, kept one centimetre apart, when a solution of one gram-molecule of the electrolyte is placed between the electrodes." The results of Ostwald's ex-

[1] *J. prakt. Chem.* (2), **30**, 93, 225 [1884].
[2] *Ibid.*, **33**, 353 [1886].

periments led him to conclude [1] that the molecular conductivities of strong monobasic acids, in aqueous solution, gradually increase as dilution increases, and asymptotically approach a maximum value. Further investigations established the following *law of dilution* for all strong monobasic acids: *the ratio of the dilutions whereat solutions of monobasic acids have equal molecular conductivities is always the same*; for instance, the molecular conductivity of a solution of formic acid is always the same, within the limits of experimental errors, as that of a solution of butyric acid when the latter is sixteen times as dilute as the former.

In his *Lehrbuch*,[2] Ostwald puts the *law of dilution* into this form. "The order of the relative affinities is independent of the dilution, and the conclusions which are drawn concerning this order from any measurements are universally valid."

In 1885, Ostwald formulated the law of dilution so that he was able to test its applicability to many acids.[1] In 1886, he showed that the same law of dilution applies, with the same constants, to solutions of many bases.[3]

In his memoir of 1885, Ostwald considered the relations between the dilutions and the conductivities of solutions of polybasic acids. He found that these acids differed considerably from the monobasis acids; in moderately concentrated solutions most of them conducted as if their ions were H and HR'', or H and H_2R'''; when the solutions became more dilute, conduction seemed to be effected by the ions H,H, and R'', or by H,H,HR''' and H,H,H, and R'''. (R'' = radical of a dibasic acid; R''' = radical of a tribasic acid.) Until a rational expression should be found for the law of dilution of monobasic acids, it was not possible, Ostwald said, to set forth in mathematical form the facts he had observed concerning the polybasic acids. "Nevertheless," Ostwald said in 1885, "one may already perceive that it will be possible to represent the dibasic acids as, in some way, the sums of two monobasic acids

[1] *J. prakt. Chem.* (2), **31**, 433 [1885]; also *Zeitsch. für physikal. Chemie*, **1**, 74, 97 [1887].

[2] *Lehrbuch der Allgemeinen Chemie*, II. (pt. 2), p. 181 [1896–1902].

[3] *J. prakt. Chem.* (2), **33**, 332 [1886].

of different conductivities. The prospect is opened of expressing numerically the separate functions of the replaceable hydrogen of the polybasic acids." [1]

I have traced the lines of some of the most important investigations which established definite connexions between electrical and chemical forces.   In 1887, these paths united to form a high road which has proved fairly sufficient for the great load of traffic it has had to carry.   The man who formed that road was Svante Arrhenius; the methods he used were set forth in a memoir on *the dissociation of substances in aqueous solution.*[2]

We have already seen that van't Hoff extended the law of Avogadro to dilute solutions in 1887, and described the results of his investigations in the following general statement.[3]

"*Equal volumes of the most different solutions, measured at the same temperature and the same osmotic pressure, contain an equal number of molecules, and that is the number which is contained in an equal volume of a gas at the same temperature and pressure.*"

To account for the apparent deviations from this law, van't Hoff introduced a factor, i, which depended on the molecular concentrations of the solutions, and assumed that some of the molecules of the dissolved substance were separated into electrically charged parts.   Chemical objections were urged against van't Hoff's conclusion, and stress was laid on the number of apparent exceptions to his law.

Arrhenius describes the purpose of his memoir (1887) as being

"to show that . . . the assumption of the dissociation of certain substances in aqueous solution is strongly supported by conclusions drawn from the electrical properties of these substances, and that a closer examination greatly lessens the objections which may be drawn against this assumption from the chemical point of view."

---

[1] *J. prakt. Chem.* (2), **31**, 460 [1885].
[2] "Ueber die Dissociation der in Wasser gelösten Stoffe," *Zeitsch. für physikal. Chemie*, **1**, 631 [1887], from the transactions of the Swedish Academy of Sciences, June and November, 1887.   Arrhenius presented a very long memoir in 1883 to the Swedish Academy, entitled *Recherches sur la Conductibilité galvanique des Electrolytes.*   A theory of the chemical reactions of electrolytes was developed in that memoir: a critical analyis of it, by Lodge, appeared in the *Brit. Ass. Reports*, 1886, p. 357.
[3] See Chapter V, p. 163.

Osmotic pressure must be thought of as caused by the impacts of the very small particles of the dissolved substance on the walls of the containing vessel; and, as the hypothesis of Clausius, extended by Hittorf, explains electrolytic phenomena by supposing that some of the molecules of an electrolyte are separated into ions which move independently of one another, it follows that a molecule which is dissociated in aqueous solution must exert a pressure equal to that which its free ions would exert. Hence Arrhenius argued:

"If one could calculate what portion of the molecules of an electrolyte is dissociated into their ions, one could also calculate the osmotic pressure by using the law of van't Hoff."

Applying the term *active* to those molecules the ions of which are supposed by the hypothesis to move independently of one another, and the term *inactive* to those whose ions are held firmly together, Arrhenius defined the *coefficient of activity* to be the ratio between the number of active molecules and the sum of active and inactive molecules in a solution. As his hypothesis asserted that dilution changes inactive into active molecules, he said that the coefficient of activity may be taken as unity for an electrolyte in infinitely dilute solution; and that, when dilution is less than this, but is so great that such disturbing influences as internal friction may be neglected, the coefficient is less than unity, and may be put as equal to the ratio between the actual molecular conductivity of the solution and the limiting value to which the molecular conductivity of the same solution approaches as dilution increases.

When the coefficient of activity, α, is known, van't Hoff's factor, i, can be calculated as follows. The factor i is equal to the ratio between the observed osmotic pressure of a substance in solution and the osmotic pressure which it would exert if it were composed only of inactive molecules.[1] If m = number of inactive molecules, n = number of active molecules, and k = number of ions produced by the dissociation of each active molecule, then

$$i = \frac{m + kn}{m + n}.$$

---

[1] Compare Chapter V, pp. 166, 169.

As $\alpha = \dfrac{n}{m+n}$, it follows that

$$i = 1 + (k-1)\alpha.$$

The value of i can be found from Raoult's determinations of the lowerings of the freezing points of solvents: if one gram-molecule of a determinate substance lowers the freezing point of one litre of water by t°, then $i = \dfrac{t^\circ}{18 \cdot 5}$.[1]

Arrhenius gave a tabular statement showing, for ninety compounds, (i) α calculated from the conductivities, as described above; (ii) i calculated from the statement $i = t^\circ/18 \cdot 5$; and (iii) i calculated from the equation $i = 1 + (k-1)\alpha$. The experimental data, taken from the work of various experimenters, were discussed by Arrhenius. The results established a close parallelism between those values of i which were based on cryoscopic determinations and those which were calculated by the help of the hypothesis of Arrhenius. This close parallelism strengthened the two assumptions which formed the basis of the hypothesis. These assumptions were: (i) the law of van't Hoff applies to all substances, including electrolytes in aqueous solution; (ii) every electrolyte in aqueous solution consists partly of molecules which are electrolytically and chemically active, and partly of inactive molecules which are changed into active molecules by dilution, so that only active molecules are present in infinitely dilute solutions.

Arrhenius applied the term *dissociation* to the separation of an electrolyte into its ions in dilute aqueous solution; he was careful, however, to indicate the difference between this process and a process of dissociation accomplished by the action of heat. The parts of an electrolyte, the ions, he said, are charged with large quantities of electricity, and cannot be appreciably separated from one another without the expenditure of much energy, whereas the products of an ordinary process of dissociation are generally separable without difficulty.

---

[1] The existence of this relation was demonstrated by van't Hoff in 1885. *Kong. Sven. Vet.-Akad. Hand.* **21** (ii), No. 17 [1886].

In the second part of his memoir, Arrhenius shows that the hypothesis of ionic dissociation explains the fact that many properties of dilute solutions of salts are additive properties, that is, are the sums of the properties of portions of the solutions. For instance, Kohlrausch showed, in 1879, that the electrical conductivities of many salt-solutions are equal to the sum of the rates of movement of the cations and the anions of the salts.[1]

Arrhenius says:

"If a salt (in aqueous solution) is entirely separated into its ions, it must be possible to express most of the properties of the salt as the sum of the properties of its ions; because, in most cases, the ions are independent of one another, and each has a characteristic individuality whatever be the nature of the other ion which is present along with it. This argument is not unconditionally applicable to most of the solutions which we actually examine, inasmuch as complete dissociation is not attained in these solutions. Nevertheless, if those salts are considered which are dissociated to the extent of 80 or 90 *per cent.*—and such are the salts of strong bases with strong acids, almost without exception—no great errors are introduced by calculating the properties on the hypothesis that the salts are completely separated into their ions."

Arrhenius then draws attention to salts which are not formed by neutralizing strong acids by strong bases, and, judging from measurements of i by the method $i = t°/18 \cdot 5$, and calculations of i by the method $i = 1 + (k-1)\alpha$, are far from being completely dissociated into their ions even in dilute aqueous solutions. The properties of these salts, in solution, are not additive in the way in which the properties of salts formed by the interactions of strong acids and strong bases are additive.

Finally, Arrhenius considers, in some detail, special cases of additive properties of salts in aqueous solution. The heats of neutralization of many salts in dilute aqueous solution are additive properties; the specific volumes and the specific gravities, the specific refractive powers, and the capillary phenomena are often additive. The electrical conductivities of many salts are additive properties; values can be found for the conductivities of many positively charged ions, and for the conductivities of many negatively charged ions; the conductivity of the replaceable hydrogen of acids is a quantity which is independent

---

[1] Kohlrausch, *Wied. Annal.*, 6, 167 [1879].

of the composition of the acid; Ostwald's law of dilution is confirmed and explained. The lowering of the freezing point of a solvent by solution therein of a salt is an additive property, and all those properties which are proportional to the lowering of freezing point—such as lowering of vapour-pressure, osmotic pressure, and isotonic coefficients—are additive properties.

The memoir published by Arrhenius in 1887 suggested many fields of inquiry: detailed examinations were demanded of the variations in the properties classed as additive; the mechanism of ionic dissociation, and the effects of various solvents on it, required to be investigated; methods had to be found for measuring the changes of energy which accompany ionization and de-ionization; and as investigations proceeded other branches of inquiry were opened. The field has been vigorously cultivated; the fruit has been rich and varied.

Let us look to some of the effects of the hypothesis of Arrhenius on the study of chemical affinity. Some months after the appearance of Arrhenius' memoir, Ostwald made use of the connexion between electrolytic dissociation and conduction as an instrument for penetrating more deeply into the meaning of the values he had assigned to acids and bases, and had called the coefficients of affinity of these compounds. Ostwald had shown these coefficients to be independent of the quality of the process performed by the acid, or by the base, and to be nearly proportional to the conductivities of the acids and bases in aqueous solution (see pp. 408–410). Looking at them in the light of the hypothesis of Arrhenius, Ostwald declared the coefficients of affinity to be measures of the degrees of dissociation of acids and bases in aqueous solution.[1] The following is an exceedingly condensed account of Ostwald's methods and reasoning.

The conductivity of a solution of an acid depends on the number of free ions present and on their velocities. If several

---

[1] Ostwald, "Ueber die Dissociationstheorie der Elektrolyte," *Zeitschr. für physikal. Chemie*, **2**, 270 [1888]; and "Ueber die Affinitätsgrössen organischer Saüren . . . ," *l. c.*, **3**, 170 [1889].

acids were completely dissociated, that part of the conductivity which depends on the velocities of the hydrogen ions would be the same for all the acids; but the different negative ions would have different effects on the other part of the conductivity. As hydrogen ions move more than five times faster than the most quickly moving negative ions, it is evident that the differences between the conductivities of completely dissociated acids cannot be very great. It is also evident that the degree of dissociation of an acid is the chief factor in determining its electrolytic conductivity. If the degree of dissociation is taken to be proportional to the conductivity, the error which is introduced cannot exceed 16 per cent. in the extremest case, and will generally be much less than that amount.

If the chemical reactions of an acid were dependent on the hydrogen ions only, all equally dissociated acids would react equally; if the reactions were dependent on the negative ions only, equally dissociated acids would react not equally but proportionally to the velocities of their negative ions. In very many actual processes, the readiness to act will be conditioned by the number and by the velocities of both ions; but, as the hydrogen ions move very much more quickly than any negative ion, the readiness to react will depend chiefly on the hydrogen ions. Hence the degree of dissociation of an acid in solution will be the factor which chiefly conditions its readiness to react chemically, and the specific character of the negative ion will play a subordinate part.

These considerations indicate the great importance of determining the degrees of dissociation of different acids in aqueous solution. The necessary data are obtained more easily and more accurately by measuring electrolytic conductivities than by any other method. The results of measurements of conductivities will also serve to determine whether the dissociation theory is capable of expressing the facts which have been established by experiments concerning electrolytes.

Ostwald stated the following six regularities which have been empirically established for aqueous solutions of electrolytes.

    1. The molecular conductivity of every electrolyte increases as dilution increases and approaches asymptotically to a maximum value.

2. When these maximum values are referred to equivalent quantities of (i) acids, (ii) bases, (iii) salts, they are of the same order of magnitude, but are not exactly equal.

3. The maximum values can be expressed as the sums of two quantities one of which depends only on the positive ions, and the other only on the negative ions.

4. The last mentioned regularity does not hold good for concentrated solutions of electrolytes, nor for weak acids and weak bases; an approximation to the rule is observed when one compares groups of salts with ions of the same valency.

5. The molecular conductivities of such badly conducting electrolytes as weak acids and weak bases increase very slowly as dilution increases. The conductivities of monobasic acids, and of monoacid bases, increase in proportion to the square roots of the degrees of dilution, that is, of the volumes.

6. The increase of molecular conductivity follows the same law for all monobasic acids and all mono-acid bases. If these electrolytes are compared at dilutions whereat the conductivities are the same fractions of the maximum values, the degrees of dilution, or the volumes, bear a constant relation to one another.

Ostwald showed that all these empirically established regularities can be deduced as necessary consequences of the theory of ionic dissociation. In making this demonstration, Ostwald began by considering the dissociation of a gas when one molecule separates into two molecules of the products of dissociation. In that case, the pressure of the undissociated portion bears a constant proportion to the square of the pressure of the two products:

$$\frac{p}{p_1{}^2} = c.$$

The pressure of a gas is proportional to its quantity, u, and is inversely proportional to the volume, v, occupied by it; in solutions, the osmotic pressure can be put as proportional to $\frac{u}{v}$, and from the foregoing equation we get

$$\frac{uv}{u_1{}^2} = c.$$

Now, if μ_∞ is the molecular conductivity of an electrolyte at infinite dilution, that is, the maximum conductivity, and if μ_v

is the molecular conductivity at the volume v, then $\dfrac{\mu_v}{\mu_\infty}$ is the fraction, u_1, of the electrolyte which is dissociated when the total quantity of the electrolyte is taken as unity; in other words, it is the degree of dissociation. The theory says that conduction is effected by the dissociated ions only, and is proportional to the number of these (other things being equal). Hence the non-dissociated portion of the electrolyte, u, is equal to $1-\dfrac{\mu_v}{\mu_\infty}$; substituting in the equation which has been given, we have

$$\frac{\mu_\infty \left(\mu_\infty - \mu_v\right)}{\mu_v^2} v = c.$$

"If the dissociation theory is correct, this equation must express all the circumstances of the electric conductivity of binary electrolytes."

Ostwald then shows, step by step, that the equation contains the six regularities which have been experimentally established for aqueous solutions of electrolytes.

The equation may be put into a form which can be numerically verified. Let $\dfrac{\mu_v}{\mu_\infty} = m$; then the equation is

$$\frac{m^2}{(1-m)v} = c.$$

This equation asserts that the constant c must have the same value for any determinate binary electrolyte, whatever may be the degree of dilution.

In applying this equation in his memoir of 1889 (for reference see foot-note, p. 416), Ostwald preferred to find values for $\dfrac{2}{c} = \gamma$. The constant γ is independent of dilution, and is conditioned only by the nature of the acid, or base; it is a measure of the readiness of the acid, or of the base, to conduct electricity and to effect chemical reactions. The physical meaning of the constant is, the dilution whereat exactly one half of the quantity of the compound is dissociated; hence, if the values of γ for

different (binary) electrolytes are compared, comparisons are made of the concentrations whereat the electrolytes are dissociated to the extent of 50 per cent. Because the constant γ has small values for strong acids and large values for weak acids, Ostwald found it more convenient to take half its reciprocal value, and to denote this by k; $k = \dfrac{1}{2\gamma}$. Finally, because some of the values of k are very small, Ostwald multiplied k by 100, putting $100k = K$. The form in which Ostwald used the equation was

$$\frac{m^2}{v(1-m)} = K.$$

The constant K is the product of factors which depend only on the composition and the constitution of the acid, or base, whose conductivity is determined.

Ostwald determined K for about 120 monobasic acids, measuring the conductivity of each at all, or at most of the dilutions such that one gram-molecular weight was dissolved in 8, 16, 32, 64, 128, 256, 512, and 1024 litres of water. The results proved the constancy of K for each acid and its independence of the degree of dilution.[1]

The statement $\dfrac{m^2}{v(1-m)} = K$ is another form of the generalization known as *Ostwald's law of dilution* (see p. 411).

In order to calculate K it is necessary to use a value for the conductivity of each acid, or base, at infinite dilution. In a short memoir published in 1888, Ostwald showed how this value can be found, with sufficient accuracy, from a knowledge of the transport-velocities of the acid radicals (anions) and the velocity of the hydrogen ions.[2]

The ratio of ionic velocities is obtained from determinations of the changes of concentration which accompany electrolysis (see Hittorf, pp. 326–328). Kohlrausch showed in 1885 that the molecular conductivities of salts

---

[1] Arrhenius has shown (*Zeitsch. für physikal. Chemie*, **2**, 284 [1888]) that the theory of ionic dissociation enables the conductivities of mixtures of electrolytes to be calculated.

[2] "Ueber die Beziehungen zwischen der Zusammensetzung der Ionen und ihrer Wanderungsgeschwindigkeit," *Zeitsch. für physikal. Chemie*, **2**, 840 [1888].

like common salt and potassium chloride attain values which are practically constant at dilutions of about 5000 litres.[1] In order to obtain the velocity of each ion, it is only necessary to divide the maximum value of the conductivity in the proportion of the ionic velocities. From determinations made with different sodium salts, and with different potassium salts, Ostwald deduced mean values for the velocities of sodium and potassium ions, and for those of several anions (acidic radicals). He obtained a probable value for the maximum conductivity of hydrochloric acid, and by deducting the mean value of the chlorine ions he found a very probable value for the velocity of the hydrogen ions. Ostwald's results led him to the conclusion that the maximum conductivity of a monobasic acid is 276 units greater (in the units employed by him) than that of its sodium salt. In order to avoid the inconvenience of measuring the conductivity of the sodium salt of an acid at a dilution so great as 5000 litres, Ostwald showed that, to obtain an approximate but sufficiently accurate value for the conductivity of a monobasic acid at infinite dilution, it is only necessary to add to the observed conductivity, at some finite dilution, a constant which is independent of the nature of the acid; and he showed how the value of this constant is found from his determinations of the velocities of various anions.

If the dissociation of a dibasic acid in aqueous solution followed the dissocation of a gas when one molecule separates into three other molecules, that is, if a dibasic acid dissociated in accordance with the scheme $H_2R'' = H + H + R''$, the dissociation-formula $\frac{m^3}{(1-m)v^2} = c$ would hold for dibasic acids. But this formula does not at all agree with the experimental data. The dissociation of a dibasic acid is the superposition of two binary dissociations, $H_2R'' = H + HR''$, and $HR'' = H + R''$. The process is complicated by the circumstance that the total quantity of the second dissociating substance is a function of the state of dissociation of the first substance, which state is itself affected by the amount of dissociation undergone at any time by the second substance.

Ostwald said:

"Fortunately, the first process $[H_2R'' = H + HR'']$ greatly predominates in the lower phases of the dissociation, until m = about 0·5, so that the values of conductivity, referred to molecular weights, conform well to the simple dissociation-formula; and it is only when dissociation in accordance with the formula $H_2R'' = H + HR''$ has affected more than half of the molecules that the process $HR'' = H + R''$ begins to be marked."

---

[1] *Wied. Annal.*, **26**, 198 [1885].

The values of K for about 100 dibasic acids were calculated by Ostwald exactly as for monobasic acids, only those values of conductivity being used for which $m < 0.5$. The maximum values of the conductivities of dibasic acids cannot be found by the method used for finding the maximum values of monobasic acids, because to do this would require a knowledge of the velocities of the ions HR″. Ostwald obtained approximate values for the maximum conductivities of dibasic acids by using certain general conclusions regarding the connexions between the compositions and the velocities of negative ions which he drew from his measurements of the velocities of a large number of these ions.[1]

The value of K for any acid is the distinguishing mark of that acid so far as those properties are concerned which are called its affinity. The data determined by Ostwald show that the affinity-constants of acids depend only on the compositions and the constitutions of these compounds, and demonstrate the possibility of calculating the conductivities of many acids from the knowledge of their constitutions, and of elucidating the the constitutions—that is, the relative arrangements of the atoms which form the molecules—from the conductivities of acids.

In the final pages of his memoir of 1889, Ostwald considers the general character of the affinity-constants of acids.[2] If the values of K are known for certain acids, the values for acids which are derived from the parent-compounds by similar processes can be calculated, to some degree of accuracy, by multiplying the values for the original acids by a factor which is roughly the same in each case. Inasmuch as the processes whereby the various derivatives are formed are never strictly analogous, the factor is not strictly constant. Nevertheless, the fact that the relations between the affinity-constants of allied acids can be roughly expressed by a systematic scheme, although varying divergences from the scheme always present themselves, shows that these constants bear some of the marks of additive properties.

---

[1] For details see Ostwald, *Zeitsch. für physikal. Chemie*, **2**, 840 [1888].
[2] *Ibid.*, **3**, 414–417 [1889].

By applying the dynamical theory of heat to the formula which expresses the dissociation of electrolytes, Ostwald came to the following conclusions.

"The natural logarithm of the dissociation-constant or affinity-constant is proportional (save for a constant) to the heat of dissociation of the acid when it separates into its ions. As the constant is shown by experience to be composed of a series of terms, which depend on the nature and the positions of the constituent atoms, so is the electrolytic heat of dissociation the sum of a corresponding number of terms, each of which is defined by the nature and the position of each particular atom. Now, in this case, the heats of dissociation are the exact measure of the quantity of work spent in separating the acidic hydrogen atom from the negative ion, as external work does not come into consideration, and the state of the substances concerned approaches very nearly to that of the ideal gas. Consequently, the heat of dissociation measures the potential, or the force-function of the atomic complex in the corresponding position; and we see that this is the sum of those values which the individual atoms contribute to the total value according to their nature and position. . . . We see the markedly constitutive property of affinity-magnitudes reduced by this result to an additive form. This happened because the influence of constitution, or of spatial position, was itself taken into account in the terms."

The values of K found by Ostwald for acetic acid and its three chlorine derivatives may be taken as examples of the effect of constitution on the affinity-constants of acids. These are the values: for acetic acid, ($CH_3.COOH$) ·0018; for monochloracetic acid, ($CH_2Cl.COOH$) ·155; for dichloracetic acid, ($CHCl_2.COOH$) 5·14; for trichloracetic acid, ($CCl_3.COOH$) about 121. The affinity-constant of the acid $CCl_3.COOH$ is about 67,000 times greater than the constant of the acid $CH_3.COOH$. These data show the great effect produced on that most important property of an acid, its affinity, by the substitution of the very negative atom of chlorine for hydrogen. Although the type is maintained, as Dumas, Gerhardt, and Laurent said, nevertheless the properties are profoundly modified, as Berzelius maintained. Hydrochloric acid, HCl, is approximately one and a half times stronger than trichloracetic acid. If these facts are translated into the language of the hypotheses of molecular structure and ionic dissociation, they assert that the substitution of chlorine atoms for non-acidic atoms of hydrogen in the molecule of acetic acid so modifies the actions and reactions of all the atoms that the hydrogen atom which is

closely associated with atoms of oxygen is very readily ionized, and that, if the ionizable atom of hydrogen is in direct union with an atom of chlorine, as it is in hydrochloric acid, the hydrogen atom is still more readily ionized.

The facts established by Ostwald concerning the connexions between the constitutions and the affinities of acids strengthen and extend the views regarding atomic arrangement and atomic affinities which had their origin in Kekulé's conception of the benzene molecule, and in Pasteur's idea of molecular asymmetry.[1]

The values of the affinity-constants of nearly fifty bases were determined by Bredig in 1894; his results confirmed Ostwald's law of dilution, and elucidated some of the connexions between the constitutions and the strengths of bases.[2]

Since the publication of Ostwald's memoir in 1889, much work has been done on the connexions between the constitutions and the conductivities of compounds. To give even a brief summary of these investigations would lead us too far afield. The student is advised to read Chapter II, "Relation of Chemical constitution to conductivity" (written by T. S. Moore), of Lehfeldt's *Electro-Chemistry*, Part I.

In 1889, after the publication of Ostwald's memoir wherein he gave values to the affinity-constants of many organic acids, and connected these values with the constitutions of the acids, van't Hoff showed[3] that the affinity which causes the combination of the ions to form an acid can be calculated from Ostwald's data, when affinity is regarded as a force, and is measured by the work which a reaction is able to do. Van't Hoff made the necessary calculations for several acids, and stated the affinities between the ions in calories. The relations between the affinity-constants of Ostwald and the constitutions of the acids are reflected, van't Hoff said, in the calorimetric values of the work done in the formation of the acids from their ions. When the affinity-constant is large, the work done in the association of the ions is small.

---

[1] See Chapter XI, especially pp. 294–297, and 309–312.
[2] *Zeitsch. für physikal. Chemie*, **13**, 289 [1894].
[3] *Ibid.*, **3**, 608 [1889].

In his *Studies in Chemical Dynamics* [1] [1895], van't Hoff showed how measurements can be made of the affinity of a chemical reaction, that is, of the force which causes the reaction in terms of the work done by the force. The meaning given by van't Hoff to the term *affinity* will be made evident by considering his presentation of the affinities concerned in a system which is characterized by having a transition-temperature, that is, a temperature whereat both portions of the system coexist in equilibrium. He instances the system

$$CuCl_4K_22H_2O \rightleftarrows CuCl_3K + KCl + 2H_2O.$$
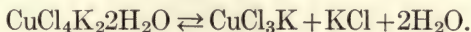
At temperatures above $92°\cdot4$ the right-hand system completely replaces the other, and below $92°\cdot4$ only the left-hand system exists. According to van't Hoff, the affinity which produces the system on the right hand of the arrows is equal, at $92°\cdot4$, to the affinity which produces the system on the left hand of the arrows; in other words, the difference between the two affinities is equal to zero at $92°\cdot4$.

After considering thermodynamically some cases of equilibrium in systems characterized by the existence of transition-temperatures, van't Hoff deduced a general expression for the work which a transition in such a system is able to perform. He said:

"The work, expressed in calories, which the affinity can accomplish in a chemical transition, at a given temperature, is equal to the quantity of heat which causes the transition, divided by the absolute temperature of the transition-point, and multiplied by the difference between that temperature and the temperature whereat the transition happens." [2]

The *Journal of Physical Chemistry* for February, 1905, contains an address by van't Hoff on the progress of physical chemistry, delivered to the *American Association for the Advancement of Science*.[3] In that address van't Hoff says that the simplest method of obtaining a measurement of the force of affinity is to reverse chemical action by pressure, and to determine the minimum pressure which is sufficient to stop the chemical transition. Burnt gypsum combines with water; but

[1] For data regarding this work see foot-note, p. 432.
[2] Translated from pp. 247, 248 of the German edition of van't Hoff's book [1896].
[3] *J. Phys. Chemistry*, **9**, 81 [1905].

this combination can be prevented by pressure. There is a limiting pressure; combination with water proceeds at any pressure less than the limiting pressure, but not at any greater pressure.

"If the chemical change takes place under a pressure only slightly less than that which would prevent it, thus practically taking place under the limiting pressure, we get out of affinity the greatest quantity of work that it can possibly produce, and this quantity is the same whatever the nature of the opposing action, be it electricity, light, or anything else. Therefore, in this maximum work we have a sound measure of affinity."

"Affinity may be defined as the maximum quantity of work that a chemical change can produce. Equilibrium ensues when this quantity is zero."

By proceeding on these lines, van't Hoff says, we are able to treat affinity-problems "without admitting anything concerning the nature of affinity, or of the matter wherein the affinity is supposed to reside."

The hypothesis of ionic dissociation has opened many subjects of great importance and interest connected with chemical affinity, which are being investigated. I will draw the reader's attention to a few of these subjects.

Ostwald's law of dilution is not consistently followed by compounds which are very largely ionized in moderately dilute solutions; to this class of compounds belong strong acids and bases, and very many salts. The affinities of these electrolytes may be compared by comparing their degrees of dissociation at each of several dilutions; but their departure from the law of dilution demands and is receiving investigation.[1]

We have seen that Ostwald calculated the affinity-constants of many dibasic acids from measurements of conductivity at dilution not exceeding that whereat the dissociation $H_2R'' = H + HR''$ happens. The second stage of dissociation of these acids is represented by the expression $HR'' = H + R''$. As a second dissociation-constant can often be found for this stage of the process, two affinity-constants are assigned to many dibasic acids. To develop methods for finding the second constant, to trace relations between the values of the two constants, and to connect both with the constitutions of dibasic acids, is

---

[1] For an account of recent work on the law of dilution, see *Chemical Society's Annual Reports on the Progress of Chemistry*, **1**, 18 [1905]; **2**, 22 [1906].

an inquiry which has been prosecuted with more or less success. Similar questions are opened, and are being investigated, by the study of the conductivities of tribasic acids.[1]

The ionic hypothesis, and the methods which it suggests for measuring affinity-constants, are completely applicable only to aqueous solutions of electrolytes. Solutions in various other solvents, especially in liquefied gases, conduct electricity rapidly; and measurements of conductivity have been made, particularly of salts and bases in liquefied sulphur dioxide and in liquefied ammonia. The difficult problem of the ionizing powers of solvents has thus been opened, but by no means solved.[2] The facts which have been observed do not indicate regular connexions between the degrees of ionization of salts on the one hand, and of the acids and bases, on the other hand, which react to form the salts. The hypothesis of electrons pictures ionization as the gain, or the loss, by an atom, of one or of more than one electron: the formation of a univalent anion is represented to be the gain of an electron, and the formation of a univalent cation to be the loss of an electron. (See Chapter XII, pp. 344, 345.) Calling readiness to ionize positively (readiness to lose electrons) the affinity of an atom for positive electricity, and meaning by the affinity of an atom for negative electricity the readiness of that atom to become an anion (to gain electrons), and considering the salt sodium acetate as an example, it has been said that the affinity of an atom of sodium for positive electricity must be the same whether the sodium forms a part of caustic soda or of sodium acetate, and that the affinity of the radical of acetic acid ($CH_3.COO$) for negative electricity must be the same whether that radical forms a part of acetic acid or of sodium acetate. Why then is an aqueous solution of sodium acetate more ionized than would be expected from the observed ionizations of caustic soda and acetic acid taken separately? Abegg and Bodländer say;[3] because the chemical force which holds sodium to hydroxyl in caustic soda is probably very different from that which binds sodium to acetyl ($CH_3.COO$) in sodium

---

[1] For an account of what has been done in these subjects, consult Lehfeldt's *Electro-Chemistry*, Part I, pp. 111–124.

[2] See Lehfeldt, *l. c.*, pp. 83–89. See also Chapter XVI.

[3] *Zeitsch. für anorgan. Chemie*, **20**, 453 [1899].

acetate, and the chemical force which binds hydrogen to acetyl in acetic acid probably differs much from that which holds sodium to acetyl in sodium acetate; and also because these chemical forces act in opposition to the affinities for electricity of the atoms and atomic groups. This hypothesis suggests and throws some light on questions concerning the electro-affinities of atoms and the constitutions and stabilities of ions; it points the way to determinations of the electro-affinities of atoms and gives glimpses of a general theory of ionization. The hypothesis of electro-affinity forms, in the hands of Abegg and Bodländer, the possible basis of a classification of inorganic compounds.[1]

Instead of opposing "chemical force" to "electro-affinity," would it not be simpler and more in keeping with the conceptions of the electron hypothesis to say that the readiness of the sodium atom to ionize positively, that is, to lose an electron without taking up a foreign electron, is not the same when caustic soda is dissolved in water as it is when sodium acetate is dissolved in water, as the readiness of the hydrogen atom to ionize positively is not the same when acetic acid is dissolved in water as it is when trichloracetic acid dissolves in water? "The electrical state of an atom, depending as it does on the power of the atom to emit or retain corpuscles, may be very largely influenced by circumstances external to the atom." (J. J. Thomson, *Electricity and Matter*.) It may even be supposed that an atom which is electropositive when uncombined with other atoms may be negative in certain molecules. (Compare Chapter XII, p. 349.)

In the present chapter, and in preceding chapters, I have traced the development of Davy's idea of the close connexion between chemical and electrical phenomena, through the electro-chemical system of Berzelian dualism to the definite expression by Faraday, in 1834, that "the forces called electricity and chemical affinity are one and the same."[2] We have followed some of the investigations which have helped to elucidate and

---

[1] A brief account of the hypothesis of Abegg and Bodländer is given in Lehfeldt's *Electro-Chemistry*, Part I, pp. 138–140.

[2] *Phil. Trans.*, **125**, 434 [1834].

to define the meaning of Faraday's words, especially the researches of Daniell, of Hittorff, of Ostwald, of van't Hoff, of Arrhenius, and of J. J. Thomson.

The proportionality of chemical affinity and electromotive force is probably most clearly realized by amplifying what Faraday said in 1834:

> "The electricity of the voltaic pile . . . is entirely due to chemical action, and is proportionate in its intensity to the intensities of the affinities concerned in its production, and in its quantity to the quantity of matter which has been chemically active during its evolution." [1]

Each form of energy has two factors; a capacity (or quantity) factor, and an intensity (or strength) factor. In the case of electrical energy, the factors are quantity of electricity, and electromotive force or difference of potential. In the case of chemical energy, the factors are quantity of matter changed as measured in equivalent weights, and chemical potential or affinity. When chemical action proceeds in a voltaic cell, the chemical energy is transformed into an equivalent quantity of electrical energy; since the quantity of electricity is proportional to the number of equivalent weights of compounds decomposed (in accordance with Faraday's law), the capacity factors of the two forms of energy are proportional. Hence, the intensity factors are also proportional; in other words, chemical affinity (in solutions of electrolytes in solvents wherein the electrolytes are ionized) is proportional to electromotive force. And, consequently, "the affinity between two reacting substances can be expressed in terms of difference of potential." [2]

It is interesting to notice that Davy's notion of varying degrees of 'exaltation of the electrical states' of substances approached what we now think of more clearly as the intensity of chemical energy. In 1807 Davy said:

> "Suppose two bodies the particles of which are in different electrical states, and those states sufficiently exalted to give them an attractive force superior to the power of aggregation, a combination would take place which would be more or less intense according

[1] Phil. Trans. 125, 434 [1834].

[2] See *Chemical Statics and Dynamics*, by J. W. Mellor, pp. 20–27 [1904].

as the energies were more or less perfectly balanced, and the change of properties would be correspondingly proportional." [1]

The outlines of the history of some of the connexions between changes of energy and material changes in systems of homogeneous substances will be sketched in the two succeeding chapters of this book.

---

[1] *Phil. Trans.* for 1807, p. 2.

CHAPTER XV.

CHEMICAL EQUILIBRIUM.

In his " Faraday Lecture," delivered in 1904, Ostwald said:

"In its original meaning, this word [equilibrium] expresses the state of a balance when two loads are of the *same weight*. Later, the conception was transferred to forces of all kinds, and designates the state when the forces neutralize one another in such a way that *no motion* occurs. As the result of the so-called chemical forces does not show itself as a motion, the use of the word has to be extended still further to mean that no variation occurs in the properties of the system. In its most general sense, *equilibrium denotes a state independent of time.*

For the existence of such a state it is above all necessary that temperature and pressure shall remain constant; in consequence of this, volume and entropy remain constant, too. Now it is a most general experimental law, that the possibility of such a state, independent of time, is dependent on the *homogeneity* of the system. In non-homogeneous bodies, as, for instance, in a solution of different concentrations in different places, or in a gaseous mixture of different composition in different places, equilbrium cannot exist, and the system will change spontaneously into a homogeneous state." [1]

If a chemical system $A + B$ reacts to produce $A' + B'$, and $A' + B'$ reacts to produce $A + B$, the distribution of the four constituents, when the whole system, $A + B + A' + B'$, attains equilibrium is the same whether the interaction begins with $A + B$, or with $A' + B'$.

He who would describe in detail the historical development of the study of chemical equilibrium must be a chemist, a physicist, and a mathematician; he must be a man of great learning, vast audacity, and much literary ability. I know that I am quite unable to attempt the task; all I wish to do is to notice a few of the salient points of the history.[2]

---

[1] *C. S. Journal*, **85**, 509 [1904].

[2] In Part II of the second volume of Ostwald's *Lehrbuch der Allgemeinen Chemie*, about 800 pages are devoted to the subject of "Chemical Equilibrium"; and the whole of the final volume (which has not yet appeared) will deal with the same subject.

If the products of a chemical change interact to re-form the original substances, the system will be in chemical equilibrium when the velocity of the direct action is equal to that of the reverse action, when the direct and reverse actions balance one another.

In his book on chemical affinity, published in 1777, Wenzel used the conception of balanced actions, but only vaguely and hesitatingly.[1] Berthollet, in 1801, applied the conception to chemical changes more in detail and with more exactitude.[1] In 1867 Guldberg and Waage based their study of chemical affinity on reactions of the type $A + B \rightleftarrows A' + 'B$, that is, reactions wherein equilibrium is attained by balancing a direct by a reverse change. They gave the equation of equilibrium, $kpq = k'p'q'$, where p, q, p' and q' are the active masses of the substances which react, and of the substances which are formed by the primary reaction, and k and k' are the forces which severally bring about the formation of the products of the primary change and the products of the reverse change. They also showed how to express the velocities of the direct and the reverse changes, and they gave an expression for the equilibrium of a system considered as the result of making these velocities equal.[2]

The law of mass action, which was clearly enunciated and applied in detail by Guldberg and Waage, has been one of the main guides in the study of chemical equilibrium. I propose to give a very brief sketch of some of the advances which have been made in the elucidation of chemical equilibrium by the help of that generalization. I wish the reader to understand that I aim at nothing more than directing attention to one or two well marked lines of progress.

In 1884, van't Hoff published his *Etudes de Dynamique chimique*. In 1885, he communicated a memoir on *the laws of chemical equilibrium* to the Royal Swedish Academy of Sciences.[3]

---

[1] For references and more details, see Chapter XIV, pp. 383, 391, 392.

[2] For a fuller treatment of Guldberg and Waage's Memoir, see Chapter XIV, pp. 400–405.

[3] "Lois de l'Equilibre chimique dans l'état dilué, gazeux ou dissous," *Kong. Sven. Vet.-Akad. Hand.*, **21** (i), No. 17 [1886]. A German translation, with notes, forms No. 110 of Ostwald's *Klassiker*.

A second, and considerably enlarged edition of van't Hoff's *Etudes* appeared in 1895. An English translation of that edition was issued in 1896, under the

Let us take one of the examples of equilibrium selected by van't Hoff in his memoir of 1885, that expressed by the statement $N_2O_4 \rightleftarrows 2NO_2$, and let us call the system, on the left side of the sign $\rightleftarrows$ the first system, and that on the right side of the sign, the second system.

"The law," van't Hoff said, "which expresses the relations that hold good, at constant temperature, in such a case, is enunciated by the following equation,

$$\frac{C_{,,}n_{,,}}{C_{,}n_{,}} = K,$$

where $C_{,,}$ and $C_{,}$ are the concentrations of the two systems, and, therefore, in our example, the quantities of $2NO_2$ and N_2O_4 per unit volume; $n_{,,}$ and $n_{,}$ are the numbers of molecules which are severally required for the transformation of the second system and of the first system: hence, in our special case, $n_{,,}=2$, and $n_{,}=1$; finally, K is a constant dependent only on temperature."

As van't Hoff said, the equation given by him is a statement of Guldberg and Waage's law of mass action, freed from the vague notion of chemical force.[1]

The case $N_2O_4 \rightleftarrows 2NO_2$ is an example of homogeneous equilibrium; there is not at any time a surface of separation between the constituents of the system. The expression $\frac{C_{,,}^{n_{,,}}}{C_{,}^{n_{,}}}$ may be used, van't Hoff said, for "heterogeneous equilibria, where solid or liquid and gaseous substances are present at the same time, provided that the dilution of the liquid or gaseous substances is sufficient for the transformations of the two systems." Taking as an example $CaCO_3 \rightleftarrows CaO + CO_2$, "the only difference in the use of the equation in such a case is that $n_{,}$ and $n_{,,}$ refer only to the gaseous substances, and, therefore, in this example, $n_{,}=0$ and $n_{,,}=1$."

The relation between the equilibrium-constant, K, and the temperature was deduced by van't Hoff from thermodynamical principles, and the expression which he obtained was proved by

---

title *Studies in Chemical Dynamics*; it is this book which is quoted here and there in the text under the reference *Studies*.

[1] Compare van't Hoff, *Berichte*, **10**, 669 [1877].

him to be in accordance with experience. The relation in question is expressed by the equation

$$\frac{d.\log \mathrm{K}}{d.\mathrm{T}} = \frac{q}{2T^2};$$

where q is the quantity of heat disengaged when the molecular quantity of the second system (taken in kilograms) is changed into the first system at constant volume, and T is the absolute temperature.

The reactions $N_2O_4 \rightleftharpoons 2NO_2$ and $CaCO_3 \rightleftharpoons CaO + CO_2$ are examples of *dissociation*.

Many instances of the decomposition by heat of compounds were known to the older chemists. In the years 1857–1866, Saint-Claire Deville made an extensive study of these processes.[1] He proved that many of the decompositions were only partial within considerable limits of temperature, unless one of the products was removed as it was formed; that if the products were not removed, they re-combined as the system cooled and the original substance was re-formed. Deville applied the term *dissociation* to all processes wherein a homogeneous substance is decomposed by heat, and is again formed when the products of the decomposition are allowed to cool in contact with each other.

Grove had shown, in 1846, that water is decomposed at a very high temperature into hydrogen and oxygen.[2] Deville found the amount of decomposition to be very small; he supposed that the quantity of water changed into hydrogen and oxygen, at a determinate temperature, was dependent on the gaseous pressure, and he introduced the notion of *dissociation-pressure*, analogous to vapour-pressure.

Debray continued the study of dissociation and enlarged its scope.[3] He found the analogy between dissociation-pressure and vapour-pressure to be very helpful; developing this analogy, he arrived at the generalization that *the pressure of the gaseous*

[1] *Compt. rendus*, **45**, 857 [1857]; **56**, 195, 729 [1864]; **59**, 873 [1865]; **60**, 317 [1865]; *Leçons sur la Dissociation* [Paris, 1866].
[2] *Phil. Trans.* **137**, 1 [1847].
[3] *Compt. rendus*, **64**, 63 [1867].

constituent, or constituents, produced in a process of dissociation, is constant at any determinate temperature, and is independent of the quantity that is decomposed of the original substance.

The writer of the article "Dissociation," [1] in *Watts' Dictionary of Chemistry* (R. T. Threlfall), says:

"Let there be a chemical system consisting of atoms of kinds, A, B, C, etc., capable of combining together in any way; let their actual state of combination at any instant depend partially on the physical conditions to which the system is exposed at the instant considered; and let the state of combination be called the state y when the physical conditions are denoted by x. Then, if y changes when x changes, in such a way that y always returns to its original value when x returns to its original value, the system is called a *dissociable system*. In fact the value of x must be independent of the 'previous history' of the system; this necessarily implies that in dissociable systems the change of state of combination must be reversible. Dissociation, therefore, is the doctrine of reversible chemical reactions. Dissociation-processes are but special cases coming under the general laws of chemical equilibrium."

Let us turn back to the equation of equilibrium given by van't Hoff. In order to make that equation strictly applicable to systems containing substances in solution, van't Hoff slightly modified its form, and wrote it thus:

$$C_{,,} \frac{\Sigma a_{,,} i_{,,}}{\Sigma a_{,} i_{,}} = \mathrm{K}.$$

Explaining this equation, van't Hoff said:

"The signification of the a is made clear by the help of the equilibrium-symbol put into the general form,

$$a_{,}' M_{,}' + a_{,}'' M_{,}'' + \text{etc.} \rightleftarrows a_{,,}' M_{,,}' + a_{,,}'' M_{,,}'' + \text{etc.},$$
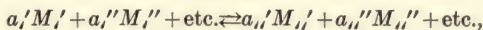
where M is the molecular formula of a compound, and a signifies the number of molecules of it that take part in the transformation. The quantity i, which appears in the expression, depends on the nature of the solvent, and on that of the compound concerned. In the case of gases, this quantity is equal to unity, and we have the equation of Guldberg and Waage. For substances dissolved in water, i is equal to the molecular lowering of the freezing-point of the solvent divided by 18·5. For solutions in various solvents, I refer to details which will follow."

---

[1] *Watts' Dictionary of Chemistry* (new edition), **2**, 388 [1889].

The meaning and some of the applications of van't Hoff's factor i have been considered in some detail in previous parts of this book.[1]

For the purpose of considering the general consequences of the relation between equilibrium and molecular concentration, van't Hoff stated the equation of equilibrium in the following form:

$$\frac{C_{//}{}^{P_{//}}}{C_{/}{}^{P_{/}}} = \text{constant},$$

where $P_{/}$ and $P_{//}$ represent the pressures of the two systems at unit concentration, the word *pressure* having the ordinary meaning in the case of gases, and meaning osmotic pressure in the case of solutions.

"If the displacement of equilibrium," van't Hoff said, "has an influence on the pressure, the latter will also have an influence on the former; whereas the second influence will not be exerted if the first condition is not fulfilled."

Analyzing this generalization, van't Hoff showed it to be in complete accord with the general statement concerning chemical equilibrium which was made by Le Chatelier [2] in 1884: "An increase of pressure causes a shifting of equilibrium to that side of the system which is at the lower pressure."

In his *Lectures on Theoretical and Physical Chemistry*, Part I (1898), p. 161, van't Hoff put the law connecting change of equilibrium and change of volume in these alternative forms.

(1) "Increase of volume favours the system possessing the greater volume.

(2) "Increase of pressure favours the system possessing the smaller volume."

Examining the (osmotic) pressures of substances in solution, van't Hoff said:

"When substances in solution are considered, the pressures $P_{/}$ and $P_{//}$ measure nothing else but the attraction for the solvent exerted by the same quantity of the matter in solution, in its two forms, called the first and the

[1] See Chapters V and XII, pp. 166 and 331, 332.
[2] *Compt. rendus*, **99**, 786 [1884].

second system. Consequently, the relation which has been obtained indicates that the displacement of equilibrium produced in a solution by varying the quantity of solvent depends, as one would expect, on the attraction which the matter in solution, in its two forms, exerts on the solvent, so that *the addition of solvent will advantage that one of the two systems whose attraction for the solvent is the greater.* This follows, from what has been demonstrated, that decrease of pressure increases the system which has the greater pressure."

The laws of equilibrium for dilute systems, whether gaseous or in solution, having been expressed by the two equations,

$$\frac{C_{\prime\prime}{}^{\Sigma a_{\prime\prime} i_{\prime\prime}}}{C_{\prime}{}^{\Sigma a_{\prime} i_{\prime}}} = K, \quad \text{and} \quad \frac{d.\log K}{d.T} = \frac{q}{2T^2},$$

van't Hoff described and used four methods for obtaining values for the factor i. These methods were: the use of the law of solubility of gaseous substances, the use of the law of vapour-pressure, the use of the law of osmotic pressure, the use of determinations of freezing-points.

After obtaining values for i for many salts, acids, and bases, and for some organic compounds, in certain solvents, van't Hoff proceeded to apply the equations of equilibrium to chemical systems in aqueous solution, first at a constant temperature and then at varying temperature.

Let the equilibrium in a system of four substances in solution, at constant temperature, be expressed by the scheme

$$a_1 M_1 + a_2 M_2 \rightleftarrows a_3 M_3 + a_4 M_4.$$
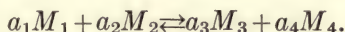
Let the several concentrations of the four substances when equilibrium is established be C_1, C_2, C_3, and C_4, and let these concentrations be the molecular quantities of the substances taken in kilograms per cubic metre of the solution. Then the original form of the law of mass action leads to the following equation of equilibrium.

$$\frac{C_3{}^{a_3} C_4{}^{a_4}}{C_1{}^{a_1} C_2{}^{a_2}} = K.$$

When van't Hoff's factor i is introduced, the equation assumes this form:

$$\frac{C_3{}^{a_3 i_3} C_4{}^{a_4 i_4}}{C_1{}^{a_1 i_1} C_2{}^{a_2 i_2}} = K.$$

Guldberg and Waage considered the equilibrium expressed by the statement,

$$CO_3Ba + SO_4K_2 \rightleftharpoons SO_4Ba + CO_3K_2.$$
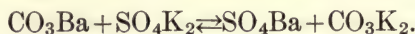
Expressing the concentrations of CO_3K_2 and SO_4K_2 by the symbols,

$$C_{CO_3K_2} \text{ and } C_{SO_4K_2}, \text{ the relation}$$

$$\frac{C_{CO_3K_2}}{C_{SO_4K_2}} = \text{constant}$$

is admitted by the law of mass action.

The value obtained by van't Hoff for i in an aqueous solution of K_2SO_4 was $2 \cdot 11$, and for K_2CO_3 in aqueous solution was $2 \cdot 26$; hence van't Hoff wrote

$$\frac{C_{CO_3K_2}^{2 \cdot 26}}{C_{SO_4K_2}^{2 \cdot 11}} = K; \quad \text{from which} \quad \frac{C_{CO_3K_2}^{1 \cdot 07}}{C_{SO_4K_2}} = \text{constant}.$$

The ratios obtained by experiment were compared by van't Hoff with those calculated by Guldberg and Waage's equation, and with those calculated by his equation. Guldberg and Waage mixed

$$BaSO_4 + QK_2CO_3 + Q_1K_2SO_4 + 500H_2O,$$
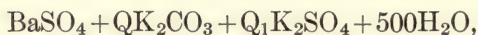
and found, when equilibrium was attained,

$$(1-x)BaSO_4 + (Q-x)K_2CO_3 + (Q_1+x)K_2SO_4 + xBaCO_3 + 500H_2O;$$
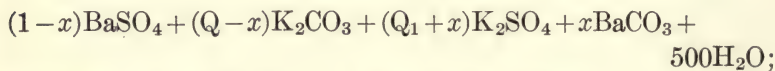
hence the two statements of the relation become

$$\frac{Q-x}{Q_1+x} = \text{constant}, \quad \text{and} \quad \frac{(Q-x)^{1 \cdot 07}}{Q_1+x} = \text{constant}.$$

Some of the results are tabulated on the next page. These results show that the values which are found by the use of van't Hoff's expression approach as nearly to a constant as those which are obtained by employing the expression of Guldberg and Waage.

Q	Q_1	x	$\dfrac{Q-x}{Q_1+x}$	$\dfrac{(Q-x)^{1\cdot07}}{Q_1+x}$
$3\cdot5$	0	$\cdot719$	$3\cdot87$	$4\cdot16$
$2\cdot5$	0	$\cdot5$	4	$4\cdot2$
2	0	$\cdot395$	$4\cdot07$	$4\cdot2$
1	0	$\cdot176$	$4\cdot68$	$4\cdot62$
2	$\cdot25$	$\cdot2$	4	$4\cdot17$
$2\cdot5$	$\cdot25$	$\cdot3$	4	$4\cdot23$
3	$\cdot25$	$\cdot408$	$3\cdot94$	$4\cdot21$
$3\cdot8$	$\cdot25$	$\cdot593$	$3\cdot8$	$4\cdot13$
2	$\cdot5$	0	4	$4\cdot2$

When Arrhenius had made it possible to calculate the concentrations of the ions in aqueous solutions of salts, of acids, and of bases (see Chapter XIV, pp. 412–414), it was only necessary to substitute the concentrations of the ions for those of the salts, acids, or bases, when the equation of Guldberg and Waage was used for expressing the equilibria of systems formed of these classes of compounds. The symbols C_1, C_2, C_3, C_4, in the equation

$$\frac{C_3{}^{a_3}C_4{}^{a_4}}{C_1{}^{a_1}C_2{}^{a_2}} = K,$$

now represented the concentrations of the ions, and the symbols a_1, a_2, a_3, a_4, expressed the numbers of ions which took part in the direct and in the reverse change.

The equation of equilibrium can be modified so as to include cases wherein the substances are only partially ionized.[1] The equation $\dfrac{d.\log K}{d.T} = \dfrac{q}{2T^2}$ does not give the exact relation between the constant, K, and the temperature, although it indicates the form of this relationship. After passing in review various attempts which had been made to elucidate the exact character of the relation between the equilibrium-constant and the temperature, van't Hoff said (*Studies* [1896], p. 217):

"The observations which have been made on the different forms of equilibrium lead to a simple general conclusion, which may be expressed in

[1] In his *Lectures on Theoretical and Physical Chemistry*, Part I [1898], van't Hoff discusses, theoretically and practically, the equilibria of solutions of non-electrolytes (pp. 113–117); the equilibria of solutions of electrolytes (pp. 117–141); the influence of temperature on homogeneous equilibria (pp. 141–148); and heterogeneous equilibria (pp. 148–159).

the following way. *Every equilibrium between two different conditions of matter (systems) is displaced by lowering the temperature, at constant volume, towards that system the formation of which evolves heat.*

This principle applies to every possible case, both of chemical and physical equilibrium. It indicates the effect of an elevation, as well as of a depression of the temperature; it expresses, finally, the fact that if no system is present the formation of which evolves heat, a change of temperature will not displace the equilibrium. This principle . . . will be called the '*principle of mobile equilibrium*' . . . "

In his *Lectures on Theoretical and Physical Chemistry*, Part I (1898), pp. 161, 162, van't Hoff expressed the principle of mobile equilibrium in these words:

"Rise of temperature favours the system formed with absorption of heat." He had shown that "change of temperature has no influence on equilibria which on displacement produce no evolution of heat, and therefore no change of temperature."

The following words, taken from van't Hoff's *Studies* (pp. 222, 223), are of great importance.

"The application of the principle of mobile equilibrium makes it possible to predict the direction in which any given chemical equilibrium will be displaced at higher or at lower temperature. Since the equilibrium is displaced, on depressing the temperature, towards those systems which are formed with evolution of heat, these will predominate at lower temperatures, while at higher temperatures they will disappear more and more, giving place to those which are formed with absorption of heat. . . . Since the temperature on the surface of the earth . . . is relatively low, about 273° above absolute zero, it is *à priori* to be expected that under ordinary conditions the majority of chemical equilibria have been displaced towards those systems which are formed with evolution of heat. This view is fully verified in all parts of chemistry. . . . If, now, chemical equilibria in general are displaced at the ordinary temperature towards the systems which are formed with evolution of heat, it is evident that *those chemical changes which occur at the ordinary temperature must in the majority of cases be accompanied by evolution of heat.*"

In 1854, Thomsen said[1] that "every simple or complex change of a purely chemical character is accompanied by evolution of heat." At a later time (1879) Berthelot formulated his *law of maximum work:*[2] "Every chemical change which is accomplished without the addition of external energy tends to the formation of that body, or system of bodies, which disengages most heat."

---

[1] See Thomsen's *Thermochemische Untersuchungen*, **1**, 12–16.
[2] See Berthelot's *Essai de mécanique chimique*, pp. 28, 29.

The principle of mobile equilibrium demonstrates that only at absolute zero is it true that "any given equilibrium will be displaced completely in the direction of the system which is formed with evolution of heat "; in other words,[1] "at the absolute zero-point, compounds formed with evolution of heat replace the others completely."

In this connexion, I quote the following pregnant remarks from Ostwald's *Lecture on the Advances of Physical Chemistry in Recent Years*, delivered in 1891.[2]

"It is generally believed that at a high temperature, such as that which exists in the electric arc and in the sun's atmosphere, all compounds must be dissociated into their elements. This view is certainly not justified. On the contrary, what we actually know about the stability of compounds is that *all compounds which are formed with an absorption of heat become more stable with rising temperature, and vice versa.* Owing to the fact that the majority of compounds known to us are formed from their elements with the evolution of heat, and, in consequence, become more unstable as the temperature rises, it has been concluded that this is generally the case. But if we remember that cyanogen and acetylene—two compounds formed with the absorption of energy—are readily formed in quantity at the high temperature of the blast furnace, and in the arc light, we see the possibility that spectra occurring at high temperatures may belong to compounds which exist only at elevated temperatures." [3]

According to Le Chatelier, van't Hoff's principle of mobile equilibrium, and the generalization that an increase of pressure causes a shifting of equilibrium towards that part of the system which is at the lower pressure, may be widened to embrace other causes which condition equilibrium, besides change of temperature and change of pressure. The "principle of the opposition of a reaction to further change " is stated by Le Chatelier as follows.[4]

"Every system in stable equilibrium which is submitted to the influence of an exterior cause that tends to produce variations in the temperature, for in the condensation (the pressure, the concentration, the number of

[1] Van't Hoff's *Lectures on Physical and Theoretical Chemistry*, Part I, p. 164 [1898].

[2] The translation of Ostwald's words is taken from Mellor's *Chemical Statics and Dynamics*, pp. 409, 410 [1904].

[3] It is interesting to notice that the transformation of radium into other forms of matter, which happens at ordinary temperatures, is accompanied by the production of large quantities of heat.

[4] *Compt. rendus*, **99**, 786 [1884]; compare Le Chatelier's "Recherches expérimentales et théoriques sur les Équilibres chimiques," *Annales des Mines* [8], **13**, 157 [1888].

molecules per unit volume) either of the whole system, or of some of its parts, can undergo only those interior changes which if they happened alone would bring about a change of temperature, or of condensation, of the opposite sign to that which results from the exterior cause.

These modifications are generally progressive and partial. They are sudden and complete only when they can happen without changing the individual condensations of the various homogeneous parts of the system in equilibrium, whilst, however, changing the condensation of the system as a whole.

They are of no effect when their occurrence cannot bring about changes analogous to that of the exterior cause. Finally, if these modifications are possible, they are not, therefore, necessary. If they do not happen, if the system remains unchanged, the equilibrium, however stable it was, becomes unstable, and can then undergo only those modifications which tend towards the conditions of stability."

There are certain cases of equilibrium which are affected in a peculiar manner by changes of temperature. The study of these equilibria led van't Hoff to the definition and application of the *transition temperature*.

Some years before the publication of van't Hoff's *Studies,* Lehmann [1] observed the occurrence of four different crystalline forms of ammonium nitrate. When the fused salt was allowed to cool, crystals belonging to the regular system formed; at about 120° these changed into rhombohedral crystals; at about 87° rhombic crystals appeared, and at the ordinary temperature another form of rhombic crystals was produced. When the fourth modification was heated it changed to the second rhombic form at about 36°; at about 87° the rhombohedral crystals appeared, and at about 120° the regular crystals were produced. Referring to these observations, van't Hoff wrote as follows.

"At the latter temperature [120°] an equilibrium exists which may be represented thus,

$$NH_4NO_3 \text{ rhombohedric} \rightleftarrows NH_4NO_3 \text{ regular.}$$
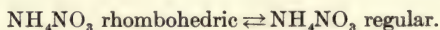
The characteristic part of the phenomenon is that, on cooling the system below 120°, the equilibrium is displaced totally towards the left-hand side of the equation; on raising the temperature above 120°, it is displaced completely towards the right. A temperature possessing properties of this kind will be called a *transition point* for the system concerned. The kind of equilibrium just described may be expected to occur when none of the substances is in the gaseous or liquid condition, that is, in so called condensed systems. The necessity of the existence of a point of transition

[1] *Zeitsch. für Krystallog.,* **1,** 106 [1877].

in such cases may be proved, quite generally, from the known laws of equilibrium."

The proof of the necessary occurrence of a transition temperature in systems containing no gaseous or liquid constituents is then given by van't Hoff (*Studies*, pp. 165–167). The examples of this phenomenon which had been investigated at the time when van't Hoff wrote (1896) are classified and considered in detail by him; methods of experiment are described and references are given to the work of various investigators (*Studies*, pp. 167–203).

The general conclusions concerning chemical equilibrium reached by van't Hoff, some of which are sketched in the preceding paragraphs, are preceded, in the *Studies*, by a classification of chemical reactions, and an investigation of examples of each class, made for the purpose of determining the relations between the velocities of the changes and the concentrations of the changing systems. For this purpose, van't Hoff divided the chemical transformations which he considered into unimolecular and multimolecular reactions. He deduced the appropriate equation for each class of reactions from the fundamental statement that, in unimolecular reactions, "there is proportionality between the quantity of substance still decomposable and the quantity which undergoes decomposition in each instant," and, in multimolecular reactions, the velocity of the change of each member of the system is proportional to its active mass, and the total change is proportional to the product of the active masses of all the changing substances.

In order to apply the foregoing statements, it is necessary to disentangle the various changes which happen in a system the initial constituents of which are known, and to trace and take into account the effects of any subsidiary changes which may occur. In other words, it is necessary, first, to determine whether a multimolecular reaction is bi-, ter-, or quadrimolecular; and, secondly, it may be necessary to divide the total reaction into parts which have been called *side* reactions, *opposing* reactions, and *consecutive* reactions.

In his *Studies*, van't Hoff described methods for determining the number of molecules which take part in a reaction from ob-

servations of the course of the reaction. The method used by van't Hoff rested on the principle that the velocity of a reaction is proportional to the nth power of the concentrations of the changing substances; or, in an equation, that

$$-\frac{dC}{dt} = kC^n,$$

where n is the number of molecules taking part in the reaction.[1]

When a solution of cane sugar is mixed with hydrochloric acid and methylacetate, two reactions happen: the cane sugar is inverted and the ester is hydrolyzed: we have here two changes taking place side by side, and we have two *side reactions*. When ethylic alcohol and acetic acid are mixed in molecular proportion, a certain quantity of ethylic acetate and a certain quantity of water are formed, and these products of the primary change react to reproduce some ethylic alcohol and some acetic acid: we have here two *opposing reactions*. When aqueous solutions of molecular proportions of ferric chloride and potassium iodide are mixed, the reaction proceeds in two stages severally represented by the equations

(1) $FeCl_3Aq + 2KIAq = FeI_2Aq + 2KClAq + ClAq,$

(2) $2KIAq + 2ClAq = 2KClAq + 2IAq.$
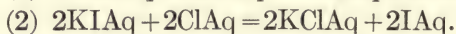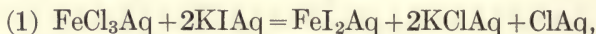
We have here two *consecutive reactions*.

Side reactions, opposing reactions, and consecutive reactions may be classified as unimolecular, bi-, ter-, etc., molecular.[2]

In the elucidation of chemical transformations, much help is given by *the principle of the co-existence of reactions*, which states that *the course of each transaction is independent of all the other transactions*.

The principle of the co-existence of reactions is stated by Ostwald as follows. [3]

---

[1] Applications of this equation are considered by van't Hoff in pp. 99–121 of *Studies*. Other methods of determining the order of molecular complexity of a reaction are described by Mellor in his *Chemical Statics and Dynamics* [1904], pp. 58–67. On pp. 415, 416 of that book Mellor says: "We are fast losing faith in the infallibility of velocity measurements as a key to the mechanism of chemical reactions."

[2] Illustrations and discussions of these classes of reactions, with references to all the most important memoirs, will be found in Mellor's *Chemical Statics and Dynamics*, pp. 71–112.

[3] *Lehrbuch*, II (ii) , p. 244. The words of the text are a free translation.

"As in the action of any number of forces on a mass, each force acts as if it alone were concerned, so it may be asserted that the course of each part of a chemical process, however complex the process may be, follows the same laws as are deduced from the study of a simple reaction. . . . "

Mellor [1] states the principle in these words.

"When a number of reactions are simultaneously taking place in the same system, each obeys the law of mass action, and each proceeds as if it were independent of the others; the total change is the sum of all the independent changes."

When a chemical change has been analyzed in the manner described above, it may still be necessary to consider, and, if possible, to eliminate, various disturbing actions, such as the influence of the medium on the velocity of the reaction. Under this heading comes the study of those cases wherein the velocity of a reaction is modified, sometimes greatly modified, by the presence of a substance which is itself unchanged at the end of the reaction; such cases are called *catalytic actions*.

In the interactions of gaseous systems, "the irregularities of the reactions are of such importance that it is frequently difficult to realize the normal course of the reaction." [2] In his *Studies* (pp. 31–42), van't Hoff measured the effects of traces of foreign gases and of moisture on reactions in certain gaseous systems. He obtained results which were not in keeping with the equations he had deduced from the law of mass action. Since the publication of the *Studies*, much work has been done by many investigators on catalytic actions, including under this heading the effects on a reaction of minute quantities of foreign substances. Many hypotheses have been tried, but the phenomena have not yet been reduced to order.[3]

The effect of the area of the surface, and of the physical nature of the surface of the walls of the containing vessels, on the velocities of certain reactions in gaseous systems, were also examined by van't Hoff.[4]

In 1801, W. Cruickshank observed that the union of hydrogen and chlorine in sunlight did not proceed very rapidly until

---

[1] *Chemical Statics and Dynamics*, p. 70.

[2] Van't Hoff's *Studies*, p. 31.

[3] See Mellor's *Chemical Statics and Dynamics*, pp. 245–352, for details and full references.

[4] *Studies*, pp. 43–50.

the mixed gases had been exposed to the light for some time.[1]
The phenomenon was rediscovered by Dalton[2] in 1811, and
again by Draper[3] in 1843; it was more fully examined in the
fifties of last century by Bunsen and Roscoe,[4] who spoke of a
"*period of photo-chemical induction.*"

In his *Studies* (p. 91) van't Hoff said:

"An exceedingly curious phenomenon is often encountered [in the first
period of a chemical change], namely, the velocity of the reaction increases
during this period, finally attaining a maximum value. The names 'chemical
induction' and 'initial acceleration' have been given to this phenomenon. . . .
Experimental investigation shows that the cause of the phenomenon is to be
found in the disturbing actions which have already been mentioned."

Having described several experiments, van't Hoff said
(*Studies*, p. 98):

"The experiments which have been described show that chemical induc-
tion, or initial acceleration, may be referred to secondary actions, and there-
fore the phenomenon may be of service in investigations relating to chem-
ical dynamics, since it indicates, in a way which is not to be undervalued,
that some necessary precaution has been omitted."

In Chapter VI of Mellor's *Chemical Statics and Dynamics*
(pp. 113–124) will be found an account of the chief experiments,
including many made by Mellor himself, on this part of the sub-
ject of the velocities of reactions, and a discussion of the results
of these experiments. Mellor says that periods of induction
may be due to the fact that *the main reaction is composed of a
number of consecutive reactions*, or to the *presence of catalytic
agents*, or to *the overcoming of passive resistance.*

If a reaction is composed of several successive reactions, then
the initial period of slow action is a necessary consequence of
the law of mass action, and "the duration of the period de-
pends on the relative magnitude of the velocity constants of
the intermediate reactions." If induction is due to the pres-
ence of a catalytic agent, the phenomenon is brought under
the general heading '*catalytic reactions*,' a class of phenomena
which awaits fuller elucidation. To say that this or that ex-
ample of induction is a case of *passive resistance*, is to class it
with other phenomena about which we have very little definite

[1] *Nicholson's Journal*, **5**, 202 [1801].
[2] *A New System of Chemical Philosophy*, **2**, 189 [1811].
[3] *Phil. Mag.* [3], **23**, 401 [1843].
[4] *Phil. Trans.*, **147**, 355, 601 [1857]; **148**, 879 [1859].

knowledge, although we can form the outlines of an hypothesis concerning them.

The phrase *passive resistance* was introduced by Willard Gibbs in his memoir *on the equilibria of heterogeneous substances* published in 1876.   In that memoir he said:[1]

"It is characteristic of all these passive resistances that they prevent a certain kind of motion or change, however the initial state of the system may be modified and to whatever external agencies of force and heat it may be subjected, within limits, it may be, but yet within limits which allow finite variations in the values of all the quantities which express the initial state of the system or the mechanical or thermal influences acting on it, without producing the change in question."

Equilibria which are caused by "the balance of the active tendencies of a system" are changed by external influences, or by changes of the initial state, even when these are infinitesimal in amount.

As the velocity of a reaction generally increases as temperature rises, and decreases as temperature falls, one may say that there is a minimum temperature for each reaction, below which the reaction either does not happen, or proceeds so slowly that its velocity cannot be determined.   At temperatures near the minimum temperature, the period of induction may be very prolonged; at slightly higher temperatures it may be shortened, but yet be long enough to be very noticeable.

A preliminary impulse may be needed to displace the equilibrium of a system, before the reaction attains its normal velocity, and different forms of energy may act in different ways in giving the necessary push.   The velocity of a change may be taken to be proportional to the available energy of the system divided by its resistance to change.   The ratio of these will vary as temperature varies;   that temperature whereat the product of available energy with the reciprocal of the resistance of a system has the maximum value, is called the optimum temperature, that is, the temperature whereat the velocity of the change is greatest.[2]

In his *Lectures*, van't Hoff devoted a few pages to the examination of "changes brought about by local causes in a sub-

---

[1] *Trans. Connecticut Acad. of Arts and Sciences*, **3**, 111 [1876].
[2] Compare Mellor's *Chemical Statics and Dynamics*, pp. 416, 417.

stance or mixture capable of reaction which then spread through-
out the mass." [1]   Speaking of this phenomenon, van't Hoff said:

"The possibility of such a propagation lies in the fact that the reaction
may bring about changes which in turn are capable of causing or accelerat-
ing the reaction.   Temperature and pressure are of the greatest importance
in this matter, and a wave of high temperature or a wave of high pressure
may be set up in a substance or mixture capable of reaction, which brings
about complete or nearly complete conversion.   The first of these is the
long-known progressive combustion taking place, for example, in gases . . . ;
the second is the explosive wave. . . . " [2]

Since the publication of van't Hoff's *Lectures*, much work
has been done on the subject of *explosions*.   I content myself
with referring the reader to Chapter XIV of Mellor's *Chemical
Statics and Dynamics*; and to a lecture delivered by H. B. Dixon
to the German Chemical Society, on "Combustion, Explosion,
and the Explosive Wave." [3]

The study of the velocities of chemical changes certainly
precedes the study of systems wherein the velocities of two
opposing changes are equal; but, as the results of the former
study find their most general expression in the laws of chemical
equilibrium, I have preferred to devote the greater part of the
first section of the present chapter to the subject of equilibrium.
The meagre sketch which is given in the preceding pages of
some of the lines on which the examination of the velocities of
chemical changes has proceeded aims at nothing more than
directing the reader's attention to the vastness of this part of
the subject of chemical equilibrium.

The subject of chemical statics and dynamics is admirably
treated, with full references to original authorities, in Mellor's
book to which I have repeatedly referred.

Hitherto I have asked the reader's attention to the de-
velopment of the study of chemical equilibrium along the lines
laid down by the law of mass action.   Inasmuch as that law
is stated in terms of a particular theory of the structure of
matter, it has not a completely universal character.   In 1869
and onwards, Horstmann attempted to apply thermodynamical

---

[1] *Lectures on Theoretical and Physical Chemistry*, Part I, pp. 243–254 [1898].
[2] *Ibid.*, p. 243.
[3] *Berichte*, **38**, 2419 [1905].

reasoning to the elucidation of chemical equilibria.[1] We have seen that van't Hoff was fairly successful in his venture in the same direction in 1886 (compare pp. 430–438).

A very lengthy memoir on equilibrium, a memoir of extraordinary importance, was published by Willard Gibbs[2] in 1874–78. I do not pretend to be able to follow the details of this very mathematical memoir; I can only indicate one or two generalizations which have had a great effect in forwarding the study and the classification of chemical equilibria.

Willard Gibbs's treatment rests on the principle that a system is in a state of equilibrium when the entropy of the system has reached a maximum value. The following is the form of the criterion of equilibrium which was most often used by Gibbs.

"For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations of the state of the system which do not alter its entropy, the variation of its energy shall either vanish or be positive."

The quantity *entropy* may be thus defined. Let Q be the quantity of heat added to a substance at constant temperature T; then $\frac{Q}{T}$ is the gain of entropy: let Q_1 be the quantity of heat lost by a substance at constant temperature T_1; then $\frac{Q_1}{T_1}$ is the loss of entropy. Let one substance at a temperature T_1 lose a quantity of heat, Q, and let this heat be gained by another substance at a lower temperature, T_2; the entropy of the hotter substance is decreased by $\frac{Q}{T_1}$, and the entropy of the colder substance is increased by $\frac{Q}{T_2}$: as $T_1 > T_2$, it follows that $\frac{Q}{T_1} < \frac{Q}{T_2}$, that is to say, the entropy of the system is increased by the passage of heat from the hotter to the colder part of it.

Gibbs developed what he called *fundamental equations*, that is, equations which express all the independent relations that are possible between the energy, entropy, volume, temperature, pressure, and quantities of the independently variable com-

[1] *Berichte*, **2**, 137 [1869]; **4**, 635 [1871].
[2] "On the equilibrium of heterogeneous systems." *Trans. Connecticut Acad. of Arts and Sciences*, **3**, 108, 343 [1874–78]. An abstract prepared by the author appeared in *Silliman's Amer. J.*, **16**, 441 [1878].

ponents of a homogeneous mass. "Upon these relations," Gibbs said, "depend a very large class of the properties of the compound considered—we may say in general, all its thermal, mechanical, and chemical properties, so far as *active tendencies* are concerned. . . ."

Having given various forms of the fundamental equations, and having shown that each is entirely equivalent to any other, Gibbs proceeded as follows (I quote from the author's abstract of the original memoir):

"In considering the different homogeneous bodies which can be formed out of any set of component substances, it is convenient to have a term which shall refer solely to the composition and thermodynamic state of any such body without regard to its size or form. The word *phase* has been chosen for this purpose. Such bodies as differ in composition or state are called different phases of the matter considered, all bodies which differ only in size and form being regarded as different examples of the same phase. Phases which can exist together, the dividing surfaces being plain, in an equilibrium which does not depend upon passive resistances to change, are called *co-existent*.

The number of independent variations of which a system of co-existent phases is capable is $n+2-r$, where r denotes the number of phases, and n the number of independently variable components in the whole system. . . . It is easily shown that if the temperature of two co-existent phases of two components is maintained constant, the pressure is in general a maximum or minimum when the composition of the phases is identical. In like manner, if the pressure of the phases is maintained constant, the temperature is in general a maximum or minimum when the composition of the phases is identical. . . . If the temperature of three co-existent phases of three components is maintained constant, the pressure is in general a maximum or minimum when the composition of one of the phases is such as can be produced by combining the other two. If the pressure is maintained constant, the temperature is in general a maximum or minimum when the same condition in regard to the composition of the phases is fulfilled."

Gibbs's memoir contained a complete thermodynamical theory of all equilibria, physical as well as chemical. He stated his theory in such abstract terms that not only were the extraordinary range and the fineness of its applications unrecognized for several years, but portions of the laws and relations which Gibbs had deduced from his theory were rediscovered by other investigators. In 1887, Roozeboom demonstrated some of the applications of Gibbs' theory to chemical equilibria.[1]

[1] "Sur les différentes formes de l'équilibre chimique hétérogène," *Rec. trav. chim. Pays-Bas.*, **6**, 262 [1887]

Books dealing with the phase rule and its applications were published by Meyerhoffer [1] in 1893, and by Bancroft [2] in 1897. Ostwald made Gibbs' memoir the basis of his treatment of chemical equilibrium in his *Lehrbuch* [3] (1896–1902). A treatise on chemical equilibrium based on the phase rule, by Roozeboom,[4] appeared in 1901. Findlay's [5] book on the phase rule was published in 1904.

The phase rule is contained in the statement which has been quoted from Willard Gibbs:

"The number of independent variations of which a system of co-existent phases is capable is $n+2-r$, where r denotes the number of phases, and n the number of independently variable components in the whole system."

One part of the work of those who have elucidated Gibbs' memoir has been to amplify, and also to define the meaning of the expressions, *phase, independently variable components of a system,* and *independent variations which a system can exhibit.* Another part of the work of the interpreters of Gibbs has been to apply his general conception in detail to many individual cases of chemical equilibrium.

Gibbs determined the degree of variability of a system in equilibrium by the relation between the number of components of the system and the number of phases existing side by side in the system. He introduced no hypotheses concerning the molecular states of the components of the phases; his results are independent of any theory of the structure of matter.

Let us consider the connotations of the terms phase, component, and degree of variability, or degree of freedom of a system.

The term *phase* refers only to the composition and thermodynamic state of a substance; ice, water, and water-vapour, for instance, are phases of water. The phases of a system are physically distinct, they can be separated mechanically. Each phase is physically and chemically homogeneous, but it is not necessarily composed of a single chemical substance; it may

---

[1] *Die Phasen-Regel und ihre Anwendungen.*

[2] *The Phase Rule.*

[3] *Lehrbuch der Allgemeinen Chemie*, vol. ii. Pt. II [1896–1902].

[4] *Die Heterogene Gleichgewichte*, bei Dr. H. W. Bakhuis Roozeboom [1901].

[5] *The Phase Rule and its applications,* by Alex. Findlay [1904].

be a mixture in solution, or a mixture of gases. A phase may be defined to be a mass of uniform concentration. The globules of butter in milk form one phase, and the aqueous solution of casein, milk-sugar, and certain other substances forms another phase; milk is a two-phase system. A glass of whisky and water is a one-phase system. Water in equilibrium with its own vapour is a two-phase system; if ice separates, the number of phases becomes three. If from melted sulphur, in equilibrium with its own vapour, there should separate both rhombic and monoclinic crystals of sulphur, the system would have four phases. As all gases are miscible in all proportions, the number of gas-phases in a system can never exceed one. In a mixture of different solids the number of distinct solids is equal to the number of phases.

The *components* of a system are those constituents of it whose concentrations can vary independently in the different phases. The system, water, ice, water-vapour, for instance, has one component, namely water (H_2O). Although water is composed of hydrogen and oxygen, united in the ratio of (approximately) 1 to 8 by weight, nevertheless hydrogen and oxygen are not components of the three-phase system, water, ice, water-vapour; for the quantity of hydrogen cannot be varied independently of the quantity of oxygen without varying the concentration of the gaseous phase.

Let there be a number of phases existing in equilibrium. If all the phases have the same composition, the system has one component. If suitably chosen quantities of two phases must be used to form all the phases which can exist, the system has two components; for instance, the system in equilibrium, $CaCO_3 \rightleftarrows CaO + CO_2$, has two components, inasmuch as the concentration of the gaseous phase, or that of either of the solid phases is given by mixing proper quantities of the other two phases. But calcium and oxygen are not components of this system, because the quantities of them cannot vary independently, nor are they in equilibrium with the system. If three phases are required to determine the composition and concentration of a fourth co-existing phase, the system has three components, and so on.

"In order to determine the number of components of any given system, it is necessary to find what phases it can form under the experimental conditions, and to ascertain the smallest possible number of substances by the addition of which all the phases can be constructed." [1]   By *addition* is meant either mixing or chemical interaction.   "The analysis is to be pushed so far, but no farther, that each phase can be represented as the sum of the components; in some cases it is necessary to take into account zero, or negative quantities of components." [2]

As an example of what is meant by zero and negative quantities of components, consider the three-phase system, $CaCO_3 \rightleftarrows CaO + CO_2$. The phase $CaCO_3$ may be represented as the sum of the phases $CaCO_3$ and CaO, if a zero value is given to the latter; the phase CaO is the sum of CaO and $CaCO_3$, the latter being taken as zero; and if a negative value is given to CaO, the gas-phase CO_2 becomes the sum of $CaCO_3$ and CaO. In this example all the phases can be represented as the sums of two components; hence the system has two components.

It is evident that the number of the components of a system is not necessarily equal to the number of the constituents of that system. Thus, the system $CaCO_3 \rightleftarrows CaO + CO_2$ has two components, but three constituents. It is sometimes possible to select different sets of components of the same system; for example, the components of an aqueous solution of Glauber's salt in equilibrium with its own vapour may be taken to be H_2O and $Na_2SO_4 10H_2O$, or H_2O and Na_2SO_4. The determination of the number of components of a system sometimes becomes a difficult task. The subject of *components and constituents* is discussed in Chapter XVIII of Bancroft's book, *The Phase Rule*.

The equilibrium of a system is determined by the relations between certain variables, prominent among which are temperature, pressure, and concentration of the components. The condition of certain systems is defined when an arbitrary value has been assigned to one of these variables. For instance, if a value is given to the pressure of the system water *plus* water-vapour, then the temperature and the concentration of the system are defined; and if a value is given to the temperature, or to the concentration, the values of the other variables are defined, be-

---

[1] Ostwald, *Lehrbuch*, II (ii), p. 478.   [2] *Ibid.*, p. 479.

cause the two phases of the system, water and vapour of water, can co-exist only when there is a certain fixed ratio between temperature, pressure, and concentration. This system is said to have one degree of freedom; it is called a *monovariant*, or, better, *univariant* system.

"The characteristics of the monovariant system are that for a given combination of phases there is for each temperature one pressure and one set of concentrations for which the system is in equilibrium; for each pressure, one temperature and one set of concentrations; for each set of concentrations, one pressure and one temperature." [1]

A determinate mass of water-vapour must occupy a certain fixed volume at a fixed pressure and temperature. If temperature only is fixed, pressure and volume may vary, within limits, without the appearance of a new phase; if pressure only is fixed, temperature and volume may vary; if volume only is fixed, pressure and temperature may vary. To define the condition of this one-phase system, values must be given to two of the determining variables. The system has two degrees of freedom, it is a *bivariant* system.

"In such a system, for a given temperature, it is possible to have a series of pressures by changing the concentrations or a series of concentrations by changing the pressures. For a given pressure the temperatures can vary with changing concentrations, and *vice versa*, while for definite concentrations there are similar relations between the pressures and temperatures." [2]

In the case of the three-phase system, ice, water, water-vapour, none of the variables can be arbitrarily changed without causing the disappearance of one of the phases. This system has no degrees of freedom; it is *non-variant;* it can exist at one pressure and one temperature only.[3]

Findlay [4] defines the number of degrees of freedom of a system to be

"the number of the variable factors, temperature, pressure, and concentration of the components, which must be arbitrarily fixed in order that the condition of the system may be perfectly defined."

[1] Bancroft, *The Phase Rule*, p. 3.
[2] *Ibid.*
[3] The terms univariant, bivariant, non-variant, multivariant, were introduced by Trevor (see *J. Phys. Chemistry*, 6, 136 [1902]).
[4] *The Phase Rule and its Applications*, p. 15.

It is evident that the degrees of freedom of a system are increased by increasing the number of components and decreasing the number of phases, and are diminished by decreasing the number of components and increasing the number of phases.

"It is possible to make a system with almost any degree of freedom; but practically, a system ceases to be interesting from the qualitative point of view when it contains less than "n" phases, because the possibilities are so numerous and so ill-defined. In the other direction, that of decreasing the components and increasing the phases, it is impossible to go." [1]

If P is the number of phases of a system, C the number of components, and F the number of degrees of freedom of the system, the phase rule states that

$$P + F = C + 2,$$
$$\text{or} \quad F = C + 2 - P.$$

The phase rule states the general conditions of equilibrium of all chemical and of all physical systems; it does not, however, enable predictions to be made of the directions of the changes which will happen when the external conditions of the systems are altered. Qualitative predictions of the direction of these changes can be made [2] by applying van't Hoff's *law of mobile equilibrium*, and Le Chatelier's *principle of the opposition of a reaction to further change*. (These statements are considered in this chapter, pp. 440–442). These two statements are expressed by Ostwald (*The Principles of Inorganic Chemistry* [1902], p. 130) in the following words:

"If a system in equilibrium is subjected to a constraint by which the equilibrium is shifted, a reaction takes place which opposes the constraint, that is, one by which its effect is partially annulled."

Bancroft's statement runs thus: [3]

"Any change in the factors of equilibrium from outside is followed by a reverse change within the system."

---

[1] Bancroft, *The Phase Rule*, p. 4.

[2] "The changes can be predicted *quantitatively*, provided the specific volumes of the phases are known, and the heat effect which accompanies the transformation of one phase into the other [is also known]." Findlay, *The Phase Rule*, p. 55, note.

[3] *The Phase Rule*, p. 4. Bancroft calls this statement "the theorem of Le Chatelier."

The classification of equilibria by the phase rule, and of changes of equilibrium by that rule and the theorems of van't Hoff and Le Chatelier, has been developed by Roozeboom, also by Bancroft, Ostwald, and many other investigators. (For references, see footnote on p. 451.)

Bancroft insists that—

"All qualitative experimental data regarding equilibrium should be presented as particular applications of the phase rule and the theorem of Le Chatelier, while the guiding principles for the classification of quantitative phenomena should be the mass law and the theorem of van't Hoff." [1]

Equilibria are generally classified in accordance with the number of components of the systems; thus, systems of one component are called systems of the first order, those with two components are called systems of the second order, and so on. Systems of the same order are divided into groups in accordance with the number of degrees of freedom, as determined by the phase rule from the number of phases.

"Systems of one component form three groups which have severally 0, 1, and 2 degrees of freedom; systems of two components form four groups with 0, 1, 2, and 3 degrees of freedom respectively; and systems of n components form $n+2$ groups with 0, 1, 2, . . . $n-1$ degrees of freedom." [2]

In some of the books which deal with applications of the phase rule, systems of the same order are classified, first, in accordance with their degrees of freedom, and, secondly, in accordance with the states of aggregation of their phases; thus, there are systems of gas-phases, systems of liquid phases, of solid phases, of gas and liquid phases, of solid and liquid phases, and systems of gas and solid phases.

To classify a system is to obtain a considerable amount of accurate knowledge concerning the conditions of its equilibrium. All non-variant systems exhibit a uniform behaviour; all univariant systems are very similar; all bivariant systems present close analogies. Hence:

---

[1] Preface to *The Phase Rule.* By "the theorem of van't Hoff," I suppose that Bancroft means the statement

$$\frac{d.\log K}{d.T} = \frac{q}{2T^2} \quad \text{(see p. 434 of this chapter).}$$

[2] Ostwald, *Lehrbuch*, II (ii), p. 303. A system of one component and three phases (for instance, water, ice, water-vapour) may exhibit fifteen arrangements of its phases.

"We are able to obtain an insight into the general behaviour of any system so soon as we have determined the number of the components and the number of the co-existing phases." (Findlay, *The Phase Rule*, p. 18.)

The connotations of the terms *solution, compound,* and *element* have been expressed in the language of the phase rule. A phase is a mass of uniform concentration; it may consist of one definite chemical substance, or the composition of it may be variable. When the limits of existence of a phase are passed, another phase is formed: as one phase is passing into another co-existent phase there may be a continuous variation of the properties of both phases, as in the evaporation of sea-water; or the properties of each phase may remain unchanged during the whole transmutation, as in the evaporation of pure water. A system which can exhibit co-existent phases the properties of which vary continuously during the change from one phase to another, is called a *solution;* this definition does not limit a solution to the ordinary cases of solids dissolved in liquids.[1] A system is called by Ostwald[2] a *hylotropic body* when the properties of each of its co-existing phases remain unchanged during the passage from one of these phases to another.

Chemically homogeneous substances may be defined in terms of the meanings given to the words *solution* and *hylotropic body.*

"A substance, or a chemical individual, is a body which can form hylotropic phases within a finite range of temperature and pressure."[3]

It is always possible to separate a solution into a finite number of hylotropic bodies (" Faraday Lecture," *loc. cit.*, p. 513); but it is not possible to transform every hylotropic body into a solution. Many hylotropic bodies can be changed into solutions, but

"There are substances which have never been transformed into solutions, or whose sphere of existence covers all accessible states of temperature and pressure. Such substances we call elements. In other words, *elements are substances which never form other than hylotropic phases.*"

[1] "By taking a solid solution to be a solid homogeneous complex of several bodies the proportion between which may vary while homogeneity is maintained, we choose an expression which corresponds with that applied to liquid solutions." Van't Hoff, *Zeitsch. für physikal. Chemie,* **24**, 648 [1897].

[2] "The Faraday Lecture; On Elements and Compounds," *C. S. Journal,* **85**, p. 511 [1904].

[3] Ostwald's "Faraday Lecture," *loc. cit.*, p. 515.

"From this we may conclude that every body is finally transformable into elements, and into only *one definite set of elements*. For the most general case is a solution. Every solution can be separated into a finite number of hylotropic components, and these again can generally be transferred into a state when they behave like solutions and can be separated further. Finally, the components remain hylotropic through the whole range of temperature and pressure, that is, they are elements. From the fact that the relation between a compound substance and its elements admits of only one qualitative and quantitative interpretation, we derive the conclusion that the resolution of any substance into its elements must always lead to the same elements in the same proportion. Here we find the source of the law of the *conservation of the elements*. This law is not generally expressed as a special stoichiometrical law, because we tacitly infer it from the atomic hypothesis. But it is truly an empirical law, and we see that it is not only a consequence of the atomic hypothesis, but also a consequence of the experimental definition of an element and of our methods of obtaining elements." [1]

Ostwald then proceeds, in his " Faraday Lecture," to deduce the quantitative laws of chemical combination from the concept of *element*, which he asserts is derivable from that of *phase*. Following Wald,[2] he holds that *phase* is a more general conception than *chemical substance*. In his wording of the meaning of the term *phase*, in the " Faraday Lecture," he speaks only of properties, but in applying the term he tacitly makes the assumption that identity of properties is accompanied by identity of composition. It seems to me that the notion of composition is implicit in the term *phase;* if this is so, no advance is made by deducing the concepts *chemical substance* and *chemical element* from a general term which has been gained by using the ideas that are deduced from it.

If we turn to Ostwald's own *Lehrbuch*, we find the following definition of hylotropic bodies.[3]

"Those substances are hylotropic which can change into other substances in such a way that the elementary composition of the product of change is the same as that of the original substance."

In developing his theory of equilibrium, Willard Gibbs started from the conception of homogeneous substances; he

[1] Ostwald's " Faraday Lecture," *loc. cit.*, pp. 516, 517.
[2] Ostwald says, in his " Faraday Lecture," that he owes to Wald the realization of the generality and the wide applicability of the concept *a phase*. In memoirs in *Zeitsch. für physikal. Chemie*, Wald dealt with the bearings of the phase rule on the classification of homogeneous substances and on the stoichiometrical laws; see especially *loc. cit.*, **22**, 259; **24**, 633 [1896, 1897].
[3] *Lehrbuch der Allgemeinen Chemie*, II (ii), p. 298 [1896–1902].

deduced the phase rule from considerations respecting "the different homogeneous bodies which can be formed out of any set of component substances." [1]

Even if it is allowed that the definitions of the chemical individual and the chemical element are obtainable from the phase rule without employing the notion of composition, I think it must be granted that the applications of these definitions to classes of chemical phenomena are made by assuming the validity of the generalization—a generalization based on experience—that identity of properties accompanies identity of composition.[2]

I do not think that the expression in the language of the phase rule of the definitions of *a chemically homogeneous substance* and *an element* leads to a finer or a more exact knowledge of the chemical relations of these two classes of substances than is obtained by using the ordinary definitions of them. Nevertheless, to group together elements and compounds as substances which can form hylotropic phases within a finite range of temperature and pressure, and to define elements to be substances which form only hylotropic phases, is to emphasize the connexions between the two sides of chemical investigation, the side which deals with the question, What is a chemically homogeneous substance? and the side which searches out answers to the inquiry, What happens when chemically homogeneous substances interact? For these definitions connect the notion of chemical homogeneity with the facts of chemical equilibrium, and the study of equilibrium is not possible until the interactions of elements and of compounds have been minutely examined.

I think it may interest the student of chemical history to read some of the forms wherein Wald expresses the bearings of the phase rule on the classification of homogeneous substances.[3]

According to Wald, *a phase* is an expression which covers all the results of the study of composition so far as definitions of chemically identical and chemically different substances are concerned.

"One must regard the phase rule in chemistry . . . as the equation of

[1] See Gibbs' abstract of his memoir in *Silliman's Amer. J.*, **16**, 441 [1878].
[2] I have tried, in the first part of this book, to trace the history of the elucidation of the connexions between composition and properties.
[3] F. Wald, *Zeitsch. für physikal. Chemie*, **24**, 647, 648 [1897].

definition of the number of components (*Bestandteile*) [of a system] which *can be recognized* under the conditions that prevail for the moment."

"Co-existent phases which comply with the requirements of the phase rule for one component are materially identical. All other bodies are chemically different. (*Stofflich identisch sind Phasen, welche koexistierend der Phasenregel für einen Bestandteil entsprechen. Alle anderen Körper sind chemisch verschieden*)."

"Chemical individuals are phases which arise (*welche . . . entstanden sind*) in a phase-system with at least one independent variation, and retain recognizably constant composition throughout all the variations that are compatible with the duration of the phase-system."

". . . for every chemical individual there must be at least one phase system, capable of variation, in which it appears without change of composition."

In the last three pages of his "Faraday Lecture," Ostwald allows himself to speculate about the transmutation of the elements. He attempts to think of chemical changes without the help of an atomic hypothesis. "What we call matter," he says, "is only a complex of energies which we find together in the same place." "The reason why it is possible to isolate a substance from a solution is, that the available energy of the substance *is a minimum*, compared with that of all adjacent bodies." The differences between substances are connected with differences between their *specific energy-content*. Could we concentrate a sufficient quantity of available energy in an element, we should probably succeed in changing it into other elements.

The applications of the phase rule and of the theorems of van't Hoff and Le Chatelier to the elucidation of equilibrium have thrown much light on many classes of phenomena. It would be outside the scope of this book to trace in detail the history of this branch of chemical physics. An examination of any of the books on the study of equilibrium will show that many of the phenomena to the elucidation of which the phase rule has been applied are more physical than chemical, and will convince the reader that the line which has been drawn, and necessarily drawn between chemistry and physics, marks a boundary that has no real existence.

CHAPTER XVI.

THE ELUCIDATION OF CHEMICAL REACTIONS BY MEASUREMENTS OF PHYSICAL PROPERTIES.

THE description of chemistry, often insisted on, as the systematic and comparative study of the changes of composition and of properties which happen in systems of homogeneous substances, makes no distinction between kinds of properties which change in these systems. The history of the gradual advance towards clearness of thinking about the molecule and the atom (Chapters IV and V); the history of the investigation of isomerism (Chapter XI), of electric conductivity as a help in chemical classification (Chapter XII), of chemical affinity and chemical equilibrium (Chapters XIV and XV); these and other parts of the history of chemical science exhibit the intimacy and the fineness of the connexions between changes that are admitted by common consent to be chemical and processes which are generally and justly called physical.

If the primary business of chemistry is to investigate the changes of properties which accompany changes of composition in certain material systems, we may legitimately suppose that this business will be advanced by inquiries into the variations of any properties, provided these variations are accompanied by changes of composition.

Investigations have proved that there are classes of physical properties which change, when composition changes, in such a way that the relations between the two kinds of variation can be quantitatively expressed when the ordinary chemical methods of presenting changes of composition are employed. To classify and elucidate these relations is the object of physical chemistry.

It is often desirable to concentrate attention on the physical

phenomena which present themselves in an examination of the values of some property which is modified by changes in the compositions of the substances that exhibit it. In investigations of this kind, secondary importance is attached to the exact relations between changes of composition and of physical properties. I think one may say that these studies belong to the domain of chemical physics.

In an address delivered in 1904 to the *American Association for the Advancement of Science,* van't Hoff says that physical chemistry is "the science devoted to the introduction of physical knowledge into chemistry, with the aim of being useful to the latter." [1]

In accordance with the plan of this book, I will confine the present chapter to descriptions of a few of the more fruitful inquiries which have been made into the relations between changes of classes of physical properties and changes of composition in the systems which exhibit these properties. This chapter is emphatically *not* a history either of physical chemistry or of chemical physics.

The differences between the energies of systems are the most general determining factors of the differences between their chemical and physical properties; it will be necessary, therefore, to notice the progress of the inquiry into the general relations between the changes of energy that determine those variations in systems of homogeneous substances which it is the business of chemistry to classify. Here again I notify the reader that I do not pretend to be writing a history of chemical energetics.

The descriptions given in this book of the progress of chemical investigation have included some account of the development of certain physical methods of inquiry, and of the employment of these methods in the elucidation of chemical reactions. The outlines have been drawn of the progress made in the examination of the relations between changes of composition and

the relative densities of gaseous substances (Chapter IV);

---

[1] *J. Phys. Chemistry,* **9,** 81 [1905].

the effects on the freezing and boiling points of solvents
of dissolving small quantities of elements and of
compounds in these solvents (Chapter V);

the osmotic pressures of dilute solutions (Chapter V);

the crystalline forms of elements and of compounds
(Chapter IV);

the electric conductivities of gases and of dilute solu-
tions (Chapters V and XII, and also XIV).

Mention has been made of some general conclusions regard-
ing the factors of energy, especially of electrical energy (Chapter
XII, pp. 335, 336; also Chapter XIV, p. 427). One far-reaching
result of the study of the connexions between thermal change
and chemical equilibrium has been referred to (Chapter XV,
p. 438).

If the chemical importance of a physical method of inquiry
is to be judged by the range of its application, and the sug-
gestiveness of the results obtained by using it, then a survey of
the past announces that among the methods of physicochemical
investigation to the history of which reference has not yet been
made in this book, there are two of great importance to chem-
istry. These two methods are severally concerned with the
study of the relations between changes of composition and
optical properties, and between thermal changes and variations
of composition, in systems of homogeneous substances.

The greater part of the present chapter is devoted to indi-
cating some of the main lines of advance in thermal and optical
chemistry. The chapter closes with a few references to the
history of chemical energetics.

Section I.

RELATIONS BETWEEN CHANGES OF COMPOSITION AND CERTAIN OPTICAL PROPERTIES OF SUBSTANCES.

When a ray of light passes from air into a medium denser
than air it is refracted towards the perpendicular; let the
angle of incidence be denoted by i, and the angle of refraction by
r, then the ratio $\dfrac{\sin i}{\sin r}$ is constant, and is called the *refractive*

index of the medium with reference to air. The refractive index of a substance is generally expressed by the Greek letter μ, sometimes by the letter n. From their measurements of the refractive indices of certain gases, made in 1807, Biot and Arago [1] concluded that the squares of the refractive indices diminished by unity are proportional to the densities of the gases examined, and that the refractive power of a mixture of gases is the sum of the refractive powers of the components, but this rule does not hold for compound gases.

When a refractive index is determined, light of one definite wave-length is used. When the medium is a single chemical substance, in the liquid state, the relative density of which is d, the quantity $\dfrac{\mu-1}{d}$ was called the *specific refractive energy* of the substance by Gladstone and Dale,[2] in 1863. Landolt,[3] in 1864, gave the names *specific molecular capacity* and *refraction-equivalent* to the product of specific refractive energy into molecular weight of the liquid compound examined.

It has been shown that more concordant results are obtained for the values of refraction-equivalents by using the formula $\left(\dfrac{\mu^2-1}{\mu^2+2}\right)\dfrac{M}{d}$, where M is the molecular weight of the liquid compound, and d is its relative density, than by employing the simple formula $\dfrac{\mu-1}{d}M$. What Landolt called refraction-equivalent is now generally called *molecular refraction*; if the substance examined is an element, the product obtained by putting the atomic weight of the element in place of M in the formula is called the *atomic refraction* of the element. The product $\left(\dfrac{\mu^2-1}{\mu^2+2}\right)d$ is generally now called the *specific refraction* of a substance. When specific refraction is determined for two rays of different wave-lengths, the difference between the values is called the *specific dispersion* of the substance. The difference

[1] *Mem. de la 1re classe de l'Institut*, **7** [1807]. A free translation into German of parts of this memoir, with annotations by Gilbert, appeared in *Gilbert's Annal.*, **25**, 345, **26**, 36 [1807].
[2] *Phil. Trans.*, **153**, 317 [1863].
[3] *Pogg. Annal.*, **123**, 595 [1864].

between the values of the molecular refraction for two rays of different wave-lengths is the *molecular dispersion* of the substance examined.

I do not propose to trace the history of the various formulæ which have been proposed and used for expressing the refractive and dispersive capacities of substances. An historical criticism of them will be found in a memoir by Brühl, published [1] in 1886. The article "Optical Methods, Section I," in *Watts' Dictionary of Chemistry* (new edition), may also be consulted (Vol. IV, pp. 221–225 [1894]).

Brühl uses the following expressions of the spectrometric constants.

$$\left(\frac{\mu^2-1}{\mu^2+2}\right)d\frac{t^\circ}{4^\circ}=\mathrm{N}=\text{specific refraction.}$$

Let μ be determined for the lines H_a and H_r, then

$$\mathrm{N}_r-\mathrm{N}_a=\text{specific dispersion.}$$

$$\left(\frac{\mu^2-1}{\mu^2+2}\right)\frac{M}{d\dfrac{t^\circ}{4^\circ}}=\mathbf{M}=\text{molecular refraction.}$$

$$\mathbf{M}_r-\mathbf{M}_a=\mathbf{N}=\text{molecular dispersion.}$$

In 1863, Gladstone and Dale [2] made an extensive inquiry into the connexions between the specific refractions and the compositions of compounds. They concluded that, with a few exceptions, "the specific refractive power of a mixture of liquids is the mean of the specific refractive powers of its constituents." They traced definite connexions between the changes of composition and the changes of specific refraction in homologous series of carbon compounds; and they founded the study of the relations between the constitutions of isomeric compounds and their refractions and dispersions, by showing that "every liquid has a specific refractive energy composed of the specific refractive energies of its component elements,

---

[1] *Berichte*, **19**, 2746 [1886].   [2] *Phil. Trans.*, **153**, 317 [1863].

modified by the manner of combination." Landolt[1] pursued the inquiry on the same lines as Gladstone and Dale, determined $\left(\frac{\mu-1}{d}\right)M$ for many compounds of carbon, and deduced values for the atomic refractions of the elements carbon, hydrogen, and oxygen.

In 1870 Gladstone[2] found values for the atomic refractions of forty-six elements from determinations of the molecular refractions of salts of these elements in aqueous or alcoholic solutions.

Both Gladstone and Landolt made use of the rule of mixtures introduced by Biot and Arago in 1807; but they recognized that the rule was not applicable to compounds unless factors were introduced depending on the manner of combination of the component elements. In a memoir published in 1905, Brühl[3] put the rule of mixtures of Biot and Arago into the form

$$100\text{N} = p\text{N}' + (100 - p)\text{N}'' \ldots ,$$

where N, N', N''. . . are the refraction or dispersion constants of a mixture and of its constituents, and p is the percentage by weight of each constituent of the mixture. Experiments have proved that the formula holds strictly only for gases; that mixing, or solution of solid or liquid substances, sometimes produces small changes in their refractive and dispersive capacities. Brühl investigated certain special cases of compounds which readily undergo isomeric change, and showed that the same values were obtained for the refractive and dispersive powers of these compounds, whether the measurements were made with the pure substances or with solutions of them in media which did not alter their chemical constitutions. If N is the specific refraction $\left(\frac{\mu^2-1}{\mu^2+2}\right)d$ of a solution of one of these compounds in a chemically inactive medium, p is the percentage by weight of the compound in the solution, N_1 is the specific

[1] *Pogg. Annal.*, **122**, 545; **123**, 595 [1864].
[2] *Phil. Trans.*, **160**, 9 [1870].
[3] Brühl and Schröder, *Zeitsch. für physikal. Chemie*, **51**, 513 [1905].

refraction of the pure solvent, and N_{11} is the specific refraction of the compound in the solution; then

$$N_{11} = \frac{100N - (100-p)N_1}{p}.$$

In the cases investigated by Brühl, the values of N_{11} determined by the formula were the same as those obtained by direct measurements of the specific refractions of the pure compounds.

A great deal of work on the connexions between the spectrometric constants and the constitutions of compounds, especially of carbon compounds, was done in the seventies, eighties, and nineties of last century by Gladstone, Landolt, Brühl, and others. The work of Gladstone, supplemented by that of Landolt, laid securely the foundations of this branch of physical chemistry. Brühl has applied, and is applying, spectrometric methods to the solution of some of the finer problems of chemical constitution and chemical interactions.

In his memoirs, published in 1886 and 1887, Brühl [1] made a more extensive examination than had been made before of the connexions between the atomic refractions of the elements in carbon compounds and the molecular refractions of these compounds. In this work Brühl showed a remarkable power of selecting the proper material for examination, a wide sweep of scientific imagination, and a vivid realization of the relative importance of the questions which presented themselves as his inquiry proceeded.

Starting with the hypothesis—the common property of all investigators who followed Gladstone and Dale and Landolt— that the spectrometric constants of a carbon compound are the sums of the constants of its constituent elements, modified by the manner of combination of these elements, Brühl laid stress upon two manners of combination, marked the distinction between two classes of isomeric compounds, by speaking of *position-isomerism* and *saturation-isomerism*.

The composition of the three isomeric compounds, propylic

[1] *Berichte*, **19**, 2746 [1886]; *Annal. Chem. Pharm.*, **235**, 1 [1886]; *Zeitsch. für physikal. Chemie*, **1**, 307 [1887].

aldelyde, acetone, and allylic alcohol, is expressed by the empirical formula C_3H_6O. The reactions and relations of these isomerides are represented by the constitutional formulæ:

$$(1) \quad H_3C\text{---}CH_2\text{---}C \underset{H}{\overset{O}{<}}$$

$$(2) \quad H_3C\text{--}\underset{\underset{O}{\|}}{C}\text{---}CH_3$$

$$(3) \quad H_2C\text{=}CH\text{---}C \underset{OH}{\overset{H_2}{<}} .$$
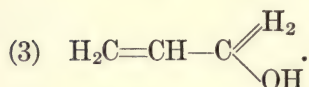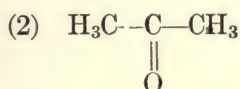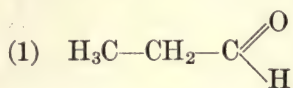
The actual valencies of the atoms in (1) are the same as the actual valencies in (2); there are two singly linked carbon-atoms and one doubly linked carbon-atom in each molecule; but the distribution of the interatomic reactions is not the same in the two molecules. Both the actual valencies and their distribution in (3) differ from the actual valencies and the distribution of them in (1) and (2). In none of the three molecules does each multivalent atom directly interact with its maximum number of other atoms; all the molecules are unsaturated. The three compounds, propylic aldehyde, acetone, allylic alcohol, are *saturation-isomerides*. The differences between the properties of saturation-isomerides may be connected with different actual valencies of the constituent atoms, and they may also be connected with different distributions of the interatomic reactions.

The reactions and relations of the three isomeric butylic alcohols (C_4H_9OH) are represented by the formulæ:

$$(1) \quad H_3C\text{---}CH_2\text{---}CH_2\text{---}CH_2OH$$

$$(2) \quad \overset{H_3C}{\underset{H_3C}{>}}CH\text{---}CH_2\text{---}OH$$

$$(3) \quad \overset{H_3C}{\underset{H_3C}{>}}C\overset{CH_3}{\underset{OH}{<}} .$$
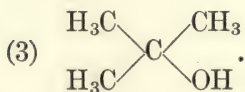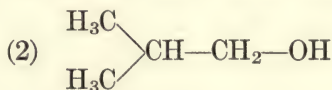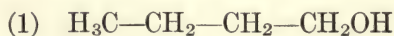
Every atom in each of the three molecules is saturated, reacts directly with its maximum number of other atoms.

These compounds are *position-isomerides*. The differences between the properties of these isomerides are connected only with different distributions of the atomic interactions.

Brühl showed that the molecular refractions of saturation-isomerides of the same composition, $C_x H_y O_z$, are not the same, but the molecular refraction of position-isomerides of the same composition, $C_x H_y O_z$, is nearly constant.

By tabulating the differences between the molecular refractions of the members of the homologous series of saturated hydrocarbons, $C_n H_{2n+2}$, Brühl found a value for the refractive capacity of the atomic group CH_2, and also for the pair of atoms H_2 (inasmuch as $C_n H_{2n+2} = nCH_2 + H_2$), and, hence, for the atom of carbon in saturated compounds. By similar methods he obtained the atomic refraction of an oxygen atom in saturated compounds, $C_x H_y O_z$. He then calculated the molecular refractions of various unsaturated carbon compounds, using the values he had found for the atomic refractions of carbon, hydrogen, and oxygen. By comparing these calculated values with those found by experiment for unsaturated compounds, Brühl deduced the numerical effect on the molecular refraction of a carbon compound of doubly linking a pair of carbon atoms; in other words, he determined the refractive value of an *ethylenic linking*—the constitutional formula of ethylene is $H_2C = CH_2$. He also deduced the refractive value of a *carbonylic linking*, $C = O$; and the numerical effect of a treble or *acetylenic linking* on the molecular refractions of compounds of carbon—the constitutional formula of acetylene is $HC \equiv CH$.

Brühl then formulated the following *fundamental law of refraction*.[1]

"The atomic refractions of carbon and oxygen are not constant, but depend upon the satisfaction of the affinities of these atoms.[2] The atomic refractions of these elements are, however, *nearly* constant, provided there is no change of saturation, and are then only very slightly conditioned by the configuration of the atoms. The univalent elements show almost invariable atomic refractions."

---

[1] *Zeitsch. für physikal. Chemie*, **1**, 340, 341 [1887].

[2] It is evident from the context that by the words *Befriedigung der Affinität* Brühl does not refer to atomic affinity but to atomic valency. I think his meaning would be best rendered in English by such words as these: *the atomic refractions of carbon and oxygen . . . depend upon the actual valencies of these atoms in different molecules.*

In a series of memoirs, from 1887 to 1905, Brühl has applied spectrometric methods to the elucidation of various problems connected with isomerism.

In Chapter XI, p. 298, I referred to Kekulé's opinion that if true constitutional formulæ are ever attained, that is, formulæ which present the actual arrangements of the parts of molecules, the goal will be reached by measuring physical properties rather than by examining chemical interactions.

Since the sixties of last century, the reactions and the properties of benzene and its derivatives have been subjected to very searching examinations. Modifications of Kekulé's formula have been proposed. The exact meaning of the hexagon formula, and of the formulæ proposed in place of it, have been eagerly discussed. One of the hypotheses suggested to explain the facts of isomerism in derivatives of benzene was, that the configuration of the atoms in the molecule C_6H_6 is not constant, but oscillates between two forms, and the properties and reactions of this compound and of its derivatives cannot be satisfactorily expressed except by assigning two formulæ to benzene.

If the atoms in the molecule of benzene have sometimes one configuration and sometimes another, then other compounds may exist the properties and reactions of which can be satisfactorily expressed only by assigning two formulæ to each of them. (Compare von Baeyer's views on the stabilities of molecules referred to on pp. 317, 318.)

The existence of compounds for which a certain constitution is suggested by one set of reactions, and another constitution is suggested by another set of reactions, has been recognized since the early eighties of the nineteenth century.[1] In the year 1885, the term *tautomeric*[2] was applied to these compounds by Laar.[3] In 1887 P. Jakobson[4] had spoken of *desmotropic*

---

[1] Compare Liebig's remarks (made in 1838) on reactions which led to different views of the constitution of the same carbon compound. (See Chapter VIII, p. 229.)

[2] ταυτό, prefix implying *the same* or *equal;* μερος=*a part, share,* or *portion·* δεσμός=*a ligature, anything that binds;* τρόπος=*way, manner,* or *fashion.* In the article "Isomerism," in *Watts' Dictionary of Chemistry* (III, p. 88 [1892]), Armstrong suggested the adjective *isodynamic* for those isomerides "which change their type with exceptional facility in the course of chemical interchanges." These compounds are often now called *dynamic isomerides.*

[3] *Berichte,* 18, 648 [1885].

[4] In a note to a communication by O. Bailter, in *Berichte,* 20, 1732 [1887], Victor

forms of compounds which easily undergo reversible isomeric change.

If a compound very easily undergoes change of atomic configuration, and if that change is reversed under slightly different conditions, it will scarcely be possible to determine the constitution of the compound by studying its chemical reactions, because the reagents used may bring about the change of configuration which it is desired to detect, and the reactions that are observed may be those of the secondary form of the compound. But, if the spectrometric constants of an unsaturated compound change when the actual valencies of its atoms alter, it may be possible to follow the changes of atomic configuration by observing the variations in the values of the spectrometric constants.

Hence it seemed that spectrometric methods of inquiry would very probably throw light on tautomeric changes, and on the formulæ to be given to compounds which exhibit peculiar and even apparently contradictory reactions.

I propose to give some account of Brühl's spectrometric investigation of benzene, and to sketch the methods used, and some of the results obtained, in his optical examination of tautomerism.

Passing over his earlier communications on benzene and compounds allied thereto, we come to Brühl's memoir published in 1894.[1]

Brühl had shown that the molecular refractions of the olefines (C_nH_{2n}) and their derivatives exceed the sum of the atomic refractions of their elements by an almost constant value, which is dependent on the number of ethylenic (double) linkings between the atoms of carbon in these compounds. He had found that benzene showed an increment of refraction nearly three times as great as that which accompanies one double linking of a pair of carbon atoms; hence Brühl concluded that the molecule of benzene contains three pairs of

Meyer says, with reference to the term *tautomerism* introduced by Laar, "P. Jakobson applies the more suitable name *desmotropy* to the phenomenon of tautomerism."

[1] *Neue Beiträge zur Frage nach der Constitution des Benzols* (*J. prakt. Chem.* [2], **49**, 201 [1894]).

doubly linked atoms of carbon. That conclusion was equivalent to asserting that "ring-closing linkings do not count spectrometrically, do not alter the molecular refraction with reference to the sum of the atomic refractions." Brühl had confirmed this conclusion by many experiments.[1] In the memoir of 1894 he says:

"It is an established fact that in homocyclic as in heterocyclic systems, closing the ring causes no increase, generally no marked change, of the spectrometric molecular constant referred to the sum of the atomic values."

Among the formulæ proposed for benzene, there are two which have been strenuously advocated by many chemists: one represents every carbon atom in direct union with four other atoms (one atom of hydrogen and three atoms of carbon); the other pictures the carbon atoms as singly linked, and assigns to each of them one "free" or "potential" valency directed towards the centre of the ring, a picture very difficult to realize vividly. The diagonal formula is presented by the first of the following symbols; the centric formula, by the second symbol.

Brühl said the diagonal linkings might, perhaps, produce the same optical effect as double linkings. His results had shown that compounds may differ in chemical type, and in molecular stability, and yet be optically similar, if the differences between them are connected with changes of distribution of atomic interactions, but had not revealed a single case of optical equivalency between compounds containing singly linked and compounds containing doubly linked carbon-atoms. As these results were confirmed by measurements of molecular volumes,[2] Brühl concluded that ethylenic linkings are never optically equivalent and never volumetrically equivalent to single ring-closing linkings.

Brühl then said: Can a centric potential valency be optically equivalent to an ethylenic linking? The most direct way of answering this question is to make a comparison of the spectro-

[1] *Annal. Chem. Pharm.*, **203**, 1 [1880]; *Zeitsch. für physikal. Chemie*, **1**, 307 [1887]; *Berichte*, **24**, 656, 3701 [1891]; **25**, 150, 1952 [1892].
[2] *Zeitsch. für physikal. Chemie*, **1**, 307 [1887].

metric constants of related compounds the constitutions of which have been established by chemical methods.

Brühl selected the following compounds.

I. *Ring Compounds.*

The sign $|{\equiv}$ is used by Brühl to denote an ethylenic linking, and the sign $|{\equiv}$ to denote an acetylenic linking.

1. Benzene, C_6H_6.

$$\begin{array}{c} CH \\ HC{\diagup}\quad{\diagdown}CH \\ HC{\diagdown}\quad{\diagup}CH \\ CH \end{array} \;|{\equiv}_3.$$

2. Benzene dihydride, C_6H_8.

$$\begin{array}{c} CH_2 \\ HC{\diagup}\quad{\diagdown}CH_2 \\ HC{\diagdown}\quad{\diagup}CH \\ CH \end{array} \;|{\equiv}_2.$$
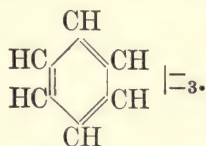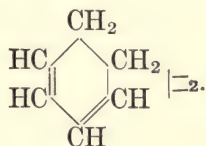
3. Benzene tetrahydride, C_6H_{10}.

$$\begin{array}{c} CH_2 \\ HC{\diagup}\quad{\diagdown}CH_2 \\ HC{\diagdown}\quad{\diagup}CH_2 \\ CH_2 \end{array} \;|{\equiv}_1.$$
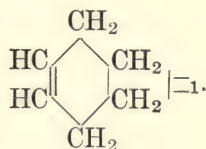
4. Benzene hexahydride, C_6H_{12}.

$$\begin{array}{c} CH_2 \\ H_2C{\diagup}\quad{\diagdown}CH_2 \\ H_2C{\diagdown}\quad{\diagup}CH_2 \\ CH_2 \end{array}$$
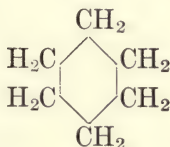
II. *Open-chain Compounds.*

5. Hexane, C_6H_{14}.

$$\begin{array}{ccccc} & H & H & H & H \\ H_3C{-}&C{-}&C{-}&C{-}&C{-}CH_3. \\ & H & H & H & H \end{array}$$

6. Hexylene, C_6H_{12}.

$$\begin{array}{cccc} & & H & H \\ H_3C{-}C=&C{-}&C{-}&C{-}CH_3. \\ H & H & H & H \end{array} \;|{\equiv}_1.$$

7. Diallyl, C_6H_{10}.

$$\begin{array}{cccc} & H & H & \\ H_2C=C{-}&C{-}&C{-}&C=CH_2. \\ H & H & H & H \end{array} \;|{\equiv}_2.$$

8. Dipropargyl, C_6H_6.

$$\begin{array}{cc} H & H \\ HC{\equiv}C{-}C{-}&C{-}C{\equiv}CH. \\ H & H \end{array} \;|{\equiv}_2.$$
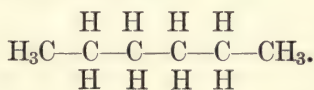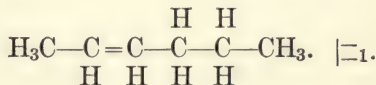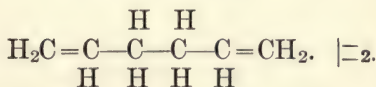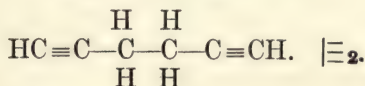
Considering the relative densities, the molecular volumes, the refractive indices, the specific refractions, and the molecular refractions and dispersions of these compounds, Brühl found that abrupt changes in the values of these physical properties happen only when there are undoubted and fundamental changes of constitution, as, for instance, in the passage from dipropargyl to diallyl, and from hexane to hexahydride of benzene. No abrupt changes of the physical properties considered are noticed in the passage from diallyl to hexylene, or from hexylene to hexane; nor in passing from benzene hexahydride to tetrahydride, then to dihydride, and then to benzene. Hence he concluded that the change of constitution in going from benzene dihydride to benzene is analogous to the change of constitution which is continuously shown in passing from benzene hexahydride to the tetrahydride and then to the dihydride, and is comparable with the change of constitution which marks the passage from hexane to hexylene and then to diallyl.

As benzene tetrahydride and dihydride do not differ from benzene in their chemical behaviour as a whole, nor in their physical behaviour, there is no ground for supposing that there are abrupt changes in the saturations of the disposable atomic valencies of these compounds. The conclusion rather is that there is one ethylenic linking in benzene tetrahydride, as there is one in hexylene, and two of these linkings in benzene dihydride as there are two in diallyl.

"The continuity of total physical behaviour which marks the progressive separation of hydrogen from hexane to diallyl on the one hand, and from benzene hexahydride to benzene on the other hand, points of necessity to continuity of change of constitution in the two series. Hence benzene must contain ethylenic linkings, and three of these if the dihydride contains two, and the tetrahydride one of these linkings. The supposition that three effective diagonal linkings, or three potential centric linkings, in benzene could produce the same physical effects as three ethylenic linkings, is quite arbitrary, and is in direct contradiction to the actual discontinuity which accompanies well known abrupt changes of constitution."

Brühl's data showed that the differences between the molecular refractions and dispersions of the saturation-isomerides benzene hexahydride and hexylene (C_6H_{12}), benzene tetrahydride and diallyl (C_6H_{10}), benzene and dipropargyl (C_6H_6), agree very closely with the differences required if the structural

formulæ on page 473 are adopted, and a ring-closing linking is considered to be optically indifferent.

If Kekulé's hexagon formula for benzene is used, the isomeric hydrocarbons anthracene and phenanthrene ($C_{14}H_{10}$) must be saturation-isomerides; if the diagonal formula or the centric formula for benzene is adopted, anthracene and phenanthrene must be position-isomerides. The molecular refraction of phenanthrene is considerably greater than that of anthracene. Inasmuch as Brühl had shown that saturation-isomerides have different molecular refractions, and the molecular refractions of position-isomerides are the same, or nearly the same, he concluded that Kekulé's formula for benzene is more in keeping with the spectrometric data than either the diagonal or the centric formula.

Whether a comparison is made of the values of various physical constants obtained experimentally for a series of compounds wherein hydrogen is successively removed from or added to benzene, or the observed molecular refractions and dispersions of these compounds are compared with the values calculated from their compositions, the conclusion is, that, "of all the structural formulæ which have been proposed for benzene, Kekulé's alone is in keeping with the facts."

Brühl says that all the results of his spectrometric experiments conclusively disprove the view expressed by von Baeyer,[1] that "the benzene nucleus can exist in two states, which are to be regarded as tautomeric, in the sense that a determinate constitution belongs to each individual derivative."

If it can be shown that derivatives of benzene—say, the phthalic acids, $C_6H_4(CO_2H)_2$—are not tautomeric, but have constitutions precisely like that of benzene, the view of von Baeyer will be untenable.   Brühl says:

"The conclusion, drawn from spectrometric investigations, that benzene, phthalic acid, and also terephthalic acid, are not tautomeric, but contain ring-systems of one and the same kind, is fully confirmed by thermo-chemical results. For, according to Stohmann's measurements, the thermal effects of successive hydrogenation of benzene, of phthalic acid, and of terephthalic acid, are completely similar, a fact which is possible only if the constitution of the benzene nucleus is alike in the three compounds."

[1] *Annal. Chem. Pharm.*, **269**, 188 [1892].

The conclusion drawn by Brühl from Stohmann's thermo-chemical examination of benzene and some of its derivatives is exactly the opposite of the conclusion drawn by Stohmann himself. Stohmann [1] regarded his results as proving that "there cannot be three equivalent double linkings in the benzene nucleus." He said that "the results of thermochemical investigation are in complete accord with the views of von Baeyer on the constitution of benzene and its derivatives."

How did Brühl reconcile his conclusion with Stohmann's experimental data?

Brühl admits the accuracy of Stohmann's work, and says that

"a similar and continuous change of thermal value accompanies the passage from hexahydro-compounds to tetrahydro- and to dihydro-compounds of benzene, whereas there is a sudden and discontinuous change of thermal value when the benzene nucleus is formed from the dihydro-compound."

But Brühl's own results proved that the change of relative density, of molecular volume, of specific and molecular refraction, and of specific and molecular dispersion, is gradual and continuous in passing from benzene hexahydride to benzene through the tetra- and the dihydride.

According to Brühl, heats of combustion are neither necessarily nor actually commensurable with other physical properties. Brühl says:

"Heat of combustion is dependent primarily on the number and nature of the atoms which compose a molecule, but it is also dependent on the mutual linkings of these atoms, on their arrangement in space, on the nature and the degree of saturation of their valencies, on the most diverse relations of strains and stresses (*von den mannigfaltigsten Spannungsverhältnissen*); in a word, it is the expression of the total energy of a body. Whereas other physical properties are manifestations of a more limited nature, are dependent chiefly on one set of conditions and to a less degree on other conditions; they are expressions of parts of the total energy. Hence such different physical constants as melting-point, boiling-point, solubility, refraction, and dispersion need not be proportional in a series of bodies; as a fact, they are often not proportional; much less is there a necessary proportionality between such constants and thermal values."

If the thermal values of the total energies of several related homogeneous substances could be analyzed so as to exhibit the

partial energy associated with a certain definite atomic arrangement, the result must be in accord with that deduced from the volumetric, from the spectrometric, and from other important properties of the substances. According to Brühl, such an analysis is practicable for benzene compounds.[1]

These are the questions to be considered: Is the presence of ethylenic groups of carbon-atoms possible or impossible in benzene compounds? If these groups may be present, what is the explanation of their specific properties in the aromatic compounds?

Brühl asserts that the conclusions to be drawn from an examination of what at first sight seem to be unimportant differences between individual thermal values, taken along with a comparative study of thermochemical results over a wide field, are entirely opposed to the conclusions which Stohmann has drawn, concerning the structure of the benzene molecule, from regarding the average values of the differences between the thermochemical data obtained by following the course of the hydrogenation of closed rings.

The dominating factors in the spectrometric behaviour of compounds of carbon are the general character of the atomic linkings—whether these are single or multiple—and the number of each kind of linking. But thermochemical relations are conditioned by the finer characters of linkings, by their stabilities, their relative positions, and by other constitutive properties of molecules. For example, the linkings in ethylenic

oxides, $\begin{array}{c} HRC\!\!-\!\!-\!\!CRH \\ \diagdown \diagup \\ O \end{array}$, cannot be optically distinguished from

the linkings in ethers, $R_2HC-O-CHR_2$; but these linkings are thermochemically different. The thermal value of a single carbon linking is conditioned by the stability of the molecule, by its state of strain (*Spannungszustand*); the single linking has different thermal values in trimethylene compounds, in tetramethylene, in pentamethylene, and in hexamethylene compounds. The differences between the thermal values of

---

[1] The development of thermochemical investigation will be considered in the next section of this chapter.

single carbon linkings may be greater than the differences between the thermal values of single and double linkings.

Ethylenic linkings also differ much thermally. It is here, Brühl asserts, that an explanation is to be found of the differences which are often noticed between the chemical behaviours and the degrees of stability of compounds that contain ethylenic linkings. The ethylene groups which are richer in energy must be more reactive, more *labile*, than those which are poorer in energy.

Although it is very difficult to disentangle thermochemical relations, yet it has become possible, Brühl says, to recognize certain regularities in the relations between the thermal equivalents of ethylene groups and the general constitutions of molecules.

"The main achievement in this department has been the elucidation of the particular nature (*Eigenart*) of the benzene nucleus, as well as the disclosure of the cause of the specific chemical characters of the aromatic compounds, and of their apparently contradictory optical and chemical behaviours."

Brühl's argument proceeds somewhat as follows. The most symmetric of several isomeric molecules is the most stable. Of isomeric unsaturated molecules which are changeable one into another, the more *labile* has always the greater heat of combustion, and the greater thermal energy accompanies ethylenic linkings in this case. When dihydrogenized benzene compounds pass into compounds of the unaltered (*intakt*) benzene nucleus, there is a sudden change of molecular stability; the change is much more marked than that which is noticed when dihydrocompounds of benzene become tetrahydrocompounds, or when a dihydro- or a tetrahydrocompound changes into its isomeride.

The line of argument which has been sketched in previous paragraphs shows that there *must* be a sudden change of thermal value in the passage from dihydrogenized benzene compounds to derivatives of benzene; that change is different from the passage from hexahydro- to tetrahydrocompounds, and from tetra- to dihydrocompounds. But this sudden change of thermal value is not inconsistent with the presence of ethylenic linkings in benzene; for these linkings must have a smaller thermal value in benzene than in hydrogenized benzenes, because they

are more stable in the former molecule. The differences between the heats of combustion of the dihydrocompounds and of derivatives of the unaltered benzene nucleus must be considerably greater than the differences between the heats of combustion of hexahydro- and tetrahydrocompounds, or than those between the thermal values of tetra- and dihydrocompounds. This conclusion is confirmed by facts established by experiment.

"Processes of addition in the aromatic and in the olefinic compounds, Brühl says, . . . consist in the loosening of ethylenic linkings and the change of these into single linkings. But the *degree of stability* of the ethylenic linkings is generally much greater in the unaltered benzene nucleus than in the hydrogenized derivatives and the olefinic compounds. The degree of stability is not the same in different classes of compounds; indeed, it varies considerably from case to case in one and the same class. Hence arise the differences between the readiness to undergo oxidation, and to form addition-products of the benzene compounds on the one hand, and their partially hydrogenized derivatives and the olefinic compounds on the other hand. . . . The immediate cause of this variation in the capacity of resistance is the difference between the energies, measurable by the thermal values, of the pairs of ethylenically linked carbon atoms. The less the thermal energy of this group, the more stable is the union of the atoms. The surprising capacity of resistance of the benzene compounds, which furnished the main reason for doubting Kekulé's hexagon-hypothesis, is quite satisfactorily explained by the proportionately smaller thermal energy of the ethylenic linkings in these compounds. It is, indeed, the thermal behaviour of the aromatic compounds which gives a substantial support to Kekulé's constitutive conception (*die constitutive Auffassung Kekulé's*), inasmuch as it removes the apparent anomalies in their chemical properties by revealing the cause of these anomalies."

Brühl says in effect that, although the linking between carbon-atoms in benzene is the same in kind as the linking in ethylene, yet the intensities of the linkings differ, and the stabilities of the molecules are not the same.

The conclusion reached by Brühl regarding the expression of the properties and reactions of benzene in a formula is, that Kekulé's hexagon formula, with alternative double and single linkings, is preferable to all other di-dimensional formulæ which have been suggested. If Kekulé's hypothesis is adopted, that the atoms of carbon oscillate in the molecule of benzene, in such a way that the first of the following formulæ represents the constitution of the molecule at one period of an oscillation, and the second formula represents the constitution at the other

period of the oscillation, an exceedingly complete presentation is given of the properties and the chemical interactions of benzene.

$$
\begin{array}{cc}
\text{CH} & \text{CH} \\
\text{CH}\diagup\text{\Large\diagdown}\text{CH} \quad & \quad \text{HC}\diagup\text{\Large\diagdown}\text{CH} \\
\text{HC}\diagdown\text{\Large\diagup}\text{CH} \quad & \quad \text{HC}\diagdown\text{\Large\diagup}\text{CH} \\
\text{CH} & \text{CH}
\end{array}
$$
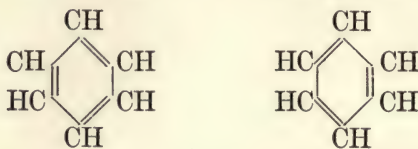
This conception of the constitution of benzene introduces a kind of structural modification which is not the same as ordinary isomerism, and differs from tautomerism. Brühl suggested the term *phasotropism.* He said: [1]

"The unaltered benzene nucleus and analogous ring-systems are *phasotropic.* The change of configuration implied by this term ceases on hydrogenation, or corresponding alteration of the system; and only isomerism, or tautomerism, in the ordinary meaning of these words, then prevails."

In a series of memoirs, published from 1894 onwards, Brühl [2] has made a spectrometric investigation of the phenomena of *tautomerism*; that is, the phenomena exhibited by certain compounds of carbon some of whose reactions suggest one structural formula, while other of their reactions seem to demand another formula. For example, in order to express the reactions of aceto-acetic ethylic ester, many chemists have deemed it necessary to assign two structural formulæ to this compound, to represent the molecule, under certain conditions, by the formula

$$
\underset{\displaystyle\ \ \overset{\|}{O}}{H_3C-C}-CH_2-\underset{\displaystyle\overset{\|}{O}}{C.O.C_2H_5,}
$$
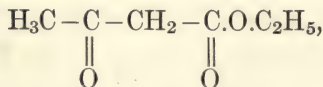
and under other conditions by the formula

$$
\underset{\displaystyle\overset{|}{OH}}{H_3C-C}=CH-\underset{\displaystyle\overset{\|}{O}}{C.O.C_2H_5.}
$$
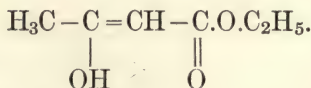
[1] "Studien über Tautomerie," *J. prakt. Chem.* [2], **50**, 218 [1894]. (Compare Knorr, *Annal. Chem. Pharm.*, **279**, 195 [1894].)

[2] "Studien über Tautomerie," *J. prakt. Chem.* [2], **50**, 119 [1894]. "Die Rolle der Medien in Lösungsvorgangen," *Zeitsch. für physikal. Chemie*, **30**, 1 [1899]. "Über tautomere Umwandlungen in Lösungen," *ibid.*, **34**, 31 [1900]. "Über Salzbildungen in Lösungen" (with H. Schröder), *ibid.*, **50**, 1 [1904]; **51**, 1, 514 [1905].

Many compounds which contain the group $\begin{matrix} -C-CH_2- \\ \parallel \\ O \end{matrix}$ can

apparently change into compounds containing the group $\begin{matrix} -C=CH- \\ | \\ OH \end{matrix}$, which again readily revert to the former type; and

certain compounds which react under some conditions as if their molecules contain the group $\begin{matrix} -C-CH- \\ \parallel \quad | \\ O \end{matrix}$, react under

other conditions as if the group $\begin{matrix} -C=C- \\ | \quad | \\ OH \end{matrix}$ were present.

That form of one of these compounds wherein the group $\begin{matrix} -C-CH_2- \\ \parallel \\ O \end{matrix}$, or the group $\begin{matrix} -C-CH- \\ \parallel \quad | \\ O \end{matrix}$, is supposed to be pres-

ent, is called the *keto-form*; the other form, containing the group $\begin{matrix} -C=CH- \\ | \\ OH \end{matrix}$, or the group $\begin{matrix} -C=C- \\ | \quad | \\ OH \end{matrix}$, is called the *enol-form*.[1]

The difference between tautomeric and ordinary isomeric phenomena is stated thus by Brühl:

"The phenomena of tautomerism consist . . . in a reciprocal capability of transformation of isomeric, labile forms, or their derivatives. Whereas ordinary stable isomerides, as propyl and isopropyl compounds, butyl and isobutyl compounds, are not autochangeable one into another (*nicht ohne Weiteres in einander überführbar sind*), the labile keto-forms are changeable into enol-forms, and these back into those."

Some chemists have supposed that the peculiar reactions of such a tautomeric compound as aceto-acetic ethyl ester require the view that both the keto-form and the enol-form of this compound are present at the same time, and the system must be regarded as in equilibrium; that if a chemical reagent is added which interacts only with the keto-form, equilibrium is dis-

[1] These terms were introduced by Brühl in 1894 ("Studien über Tautomerie"). The group $C=O$ in *keto-forms* is characteristic of ketones: a pair of doubly linked carbon-atoms, one of which is also linked to hydroxyl, is characteristic of vinyl alcohol or æthenol, $\begin{matrix} H_2C=CH \\ | \\ OH \end{matrix}$; hence the expression, *enol-form*.

turbed and the enol- changes into the keto-compound; if a
reagent is added which interacts only with the enol-form, more
of the keto-compound is changed in the endeavour of the system
to attain equilibrium; and that, for these reasons, the mixture
of the two forms reacts sometimes as if the keto-compound were
alone present, sometimes as if only the enol-compound were
present.[1]

Other chemists have supposed that the forms of a tautomeric
compound have no definite molecular constitutions, but are
to be thought of as collocations of atoms which oscillate between
certain different groupings.[2] This view has been contradicted
by the results of various investigations, notably by the work
of Perkin on magnetic rotation.[3]

It is evidently impossible to follow the course of a tauto-
meric change by using ordinary chemical reactions. But Brühl
has shown that these processes may be followed by using spec-
trometric methods of examination, because nothing is done
that can alter the molecular constitution of the substance which
is being investigated.[4]

In his *Studien über Tautomerie* [1894], Brühl considered
especially the tautomerism of ketonic, and pseudo-ketonic, that
is, enolic compounds $(C_mH_{2m+2}O_n) - xH_2$.

Analysis of the change of the group $-\overset{\overset{\displaystyle H}{|}}{C}-C=O$ to the group

$\overset{\overset{\displaystyle OH}{|}}{C}=C-$ shows that the migration of the hydrogen atom is

accompanied by the change of a carbonylic to a hydroxylic
linking, and by the formation of an ethylenic linking. The
first of these alterations of linking is attended by a decrease,
the second by an increase of the values of the spectro-
metric constants; the total optical effect is an increase of these

[1] Compare Nernst, *Theoretische Chemie*, 531 [1898].
[2] Compare Laar, *Berichte*, 18, 648 [1885]; 19, 730 [1886].
[3] "The Magnetic Rotation of Compounds supposed to contain acetyl, or to be of ketonic origin," by W. H. Perkin, *C. S. Journal*, 61, 800 [1892].
[4] Brühl, *Berichte*, 25, 366 [1892].

constants. Molecular refraction is influenced, sometimes considerably influenced by temperature; but molecular dispersion is but little affected by changes of temperature.[1] Brühl shows that measurement of the molecular dispersion of a tautomeric compound under different conditions is a very delicate instrument for detecting enolization, or ketonization, although it is not suited for determining the amount of tautomeric change. When the enol-form of one of the tautomeric compounds examined by Brühl is heated, ketonization proceeds, and can be followed by spectrometric experiments. If Laar's hypothesis is correct, that the desmotropic forms of a tautomerizable compound are merely stages in the oscillations of the atoms, such a compound cannot either ketonize or enolize on warming; either retardation or acceleration of the atomic oscillations may happen, but there cannot be a change of constitution in one definite direction. As his results clearly indicated determinate changes of constitution, Brühl concluded that Laar's hypothesis, if not untenable, is certainly inapplicable to the compounds which he examined.

Brühl's results, recorded in the memoir we are considering, seem to me to indicate that, as the phenomena of tautomeric change which he observed are instances of genuine isomerism, it is better to use the term *desmotropism* than the term *tautomerism*. The keto- and the enol-forms of the compounds examined by Brühl were shown to have different and definite constitutions: they are not forms of the same compound; they are not constituted of *the same parts*, as the word *tautomeric* implies; the differences between them are dependent on differences of linking, they are *desmotropic* differences. The only reason why a special term should be used is, that desmotropic changes are reversible without introducing foreign substances into the systems.[2]

Brühl concludes his *Studien über Tautomerie* with a reservation. His conclusions are based on the results of spectrometric experiments only. He says:

---

[1] Brühl, *Zeitsch. für physikal. Chemie*, **7**, 140 [1891].
[2] The *Brit. Ass. Reports* for 1904, p. 1, contain a résumé of recent work on the subject of dynamic isomerism, by T. M. Lowry.

"There is no single infallible chemical method of investigation; neither can there be any one infallible physical method."

We come now to Brühl's memoir, entitled *Die Rolle der Medien in Lösungsvorgangen*.[1]

In the chapter on *Chemical Affinity*, attention was directed to the fact that some compounds, which are electrolytes when dissolved in water, do not conduct electricity when dissolved in certain other solvents. (See especially p. 427.)

The advances made of late years in applying the theory of ionization make it certain that the part played by the solvent is not merely physical. The dissociation of compounds in aqueous solutions is generally more complete than their dissociation in solutions of organic solvents. What is the action of water; what are the actions of other solvents?

From his study of hydrogen peroxide,[2] made in 1895, Brühl concluded that the great dissociating power of water is connected with the chemical character of that compound. He found that the dissociating powers of certain media which do not contain oxygen are very small. He supposed that the dissociating powers of solvents which are compounds of oxygen are connected with the valency of the oxygen atom, to which he assigned a potential quadrivalency.

In 1896 H. P. Cady proved that solutions in liquid ammonia conduct rapidly.[3] About the same time it was shown by Dutoit and Aston,[4] and by Dutoit and Fridrich,[5] that nitrogen compounds as a class behave similarly to oxygen compounds with respect to dissociating power. Brühl connected the dissociating power of compounds of nitrogen with the fact that, although nitrogen is very often tervalent, it can also act as a quinquivalent atom. He suggested that many multivalent atoms would be found to act like the atoms of oxygen and of nitrogen; in other words, that compounds of multivalent atoms would cause dissociation of substances dissolved in them.[6] This conclusion was strengthened by the announcement, made in 1899 by

---

[1] *Zeitsch. für physikal. Chemie*, **30**, 1 [1899].
[2] *Ibid.*, **18**, 514 [1895].
[3] *J. phys. Chemistry*, **1**, 797 [1896–7].
[4] *Compt. rendus*, **125**, 240 [1897].
[5] *Bull. Soc. Chim.* [3], **19**, 321 [1898].
[6] *Zeitsch. für physikal. Chemie*, **27**, 319 [1898].

Kahlenberg and Lincoln,[1] that solutions of certain compounds in arsenious chloride conduct rapidly.

Further investigations showed that solutions of certain salts in phosphorous chloride are non-conductors, although solutions of the same salts in arsenious chloride conduct rapidly; and that solutions of certain other salts in phosphorous chloride conduct. Arsenious chloride acts as a dissociating and ionizing medium towards some salts; it behaves differently towards other salts.

Looking at these results of investigation, and at other results similar to these, Brühl concluded that ionizing power [2] is dependent both on the nature of the solvent and on the nature of the dissolved compound. No absolute measure of the ionizing powers of different media has been found. Besides the chemical interchanges between solvent and dissolved substance, the degree of association, the ionic friction, the specific viscosity of the medium, and other conditions come into play. Nevertheless, the dependence is unmistakable of the dissociating power of a solvent on its chemical composition, especially on its oxygen or nitrogen content. Brühl remarks that the potential valencies of some atoms do not seem to produce the physical changes which are effected, according to his hypothesis, by the potential valencies of the oxygen and the nitrogen atoms. Carbon bisulphide, olefines, and aromatic compounds are very feeble dielectrics and dissociating media, although "disposable affinities" are present in the molecules of all of them.

The hypothesis suggested by Brühl is to this effect.

"Only such media can be good dielectrics and dissociators wherein disposable chemical affinities are found; these physical properties are expressions of the chemical attracting capacities of unsaturated multivalent atoms."

This statement is not to be taken as implying that all compounds which contain disposable valencies, in accordance with the prevailing conceptions of valency, are therefore good dielectrics and dissociators.

In another part of his memoir Brühl says that, when he

---

[1] *J. phys. Chemistry,* **3**, 12 [1899].
[2] Brühl uses the expression *die ionisierende Kraft,* I have rendered this by the words *ionizing power.*

speaks of the oxygen atom as "potentially quadrivalent," he does not ascribe to it "four complete, as it were unchangeably fixed units of valency." It is sufficient for his purpose to suppose that "the affinity of oxygen is not completely exhausted by binding two hydrogen atoms or their equivalent; that arrears of affinity remain (*dass also Affinitätsreste zurückgeblieben sind*").

In order to test his hypothesis, Brühl followed spectrometrically the desmotropic changes of certain compounds in different solvents. He selected compounds each of which exists in an enol- (or α) form and in a keto- (or β) form, and exhibits considerable change of spectrometric constants when it passes from one form to the other. The enol-form had always larger refractive and dispersive powers than the keto-form. Measurements were made at the ordinary temperature, for the purpose of preventing any direct effect on the optical constants of added thermal energy. The concentrations of the solutions were definite, and practically the same for each compound. Measurements of refractive indices, and of relative densities, and hence of molecular refractions and molecular dispersions, were made with freshly prepared solutions, and also at determinate intervals of time. The same optical constants were determined for each solvent and for each compound; if the compound was a solid, it was melted and the constants were then determined. The solvents used were chloroform, benzene, carbon bisulphide, α-bromonaphthalene, ethylic alcohol, and methylic alcohol. By varying the concentrations of each solution, the effect on the desmotropic change was determined of variations in the relative masses of solvent and dissolved compound.

Brühl's results showed, first, that in none of the compounds examined did the enol-form spontaneously change into the keto-form; secondly, certain solvents produced no ketonizing effect even after seventy-five days, unless the solutions were made very dilute, and even then the amount of change was very small; thirdly, the effects of those solvents which caused ketonization were noticeable only after a considerable interval of time. There was practically no ketonization in solutions in chloroform: if the solutions were very dilute, a very little

of the keto-form was produced after a long time; ketonization proceeded very slowly in dilute solutions in benzene, carbon bisulphide, and α-bromonaphthalene; enol-compounds dissolved in methylic or in ethylic alcohol were completely changed into keto-compounds after sixty-two days.

"The investigation shows," Brühl said, "that not only does the velocity of reaction vary much with the nature of the medium, but also that a state of equilibrium between the two desmotropic forms does not exist in the solutions."

The latter part of the foregoing statement was fully confirmed by Brühl and Schröder in 1905. Their spectrometric examination of the changes of several enolic compounds into the corresponding ketonic compounds conclusively contradicted the supposition that solutions of tautomerizable compounds always contain enol- and keto-forms in equilibrium.[1]

The action of solvents like chloroform, that is, solvents with very small dissociating powers, is thought of by Brühl as comparable with the action of a vacuum in evaporation. Such solvents, he says, probably separate the crystalline aggregates of solid enolic compounds into molecular complexes, or even into single molecules, but they cause little or no ionization. When an enolic compound is dissolved in a solvent like benzene, that is, in a solvent which ionizes slightly, and the solution is diluted, a few molecules of the dissolved compound will be ionized. As enolic compounds are very weak acids, they ionize into hydrogen and a complex anion; the hydrogen ion will be attracted towards the ethylenic linking in the anion, a single linking will be formed, and at the same time a carbonylic linking will take the place of the hydroxylic linking in the original enol. The result will be the formation of the keto-form of the compound. The removal, by ketonization, of some of the enolic compound, will destroy the equilibrium of the system; ionization and ketonization will proceed until the whole of the enol-form has disappeared, and the system consists of the ketonic compound only. The greater the ionizing power of the solvent, the more quickly will the process of ketonization be finished.

[1] "Über Salzbildungen in Lösungen, III.," *Zeitsch. für physikal. Chemie*, **51**, 514 [1905].

Brühl represents the ionization and ketonization of the enolic compound α-ethylmesityloxidoxalate by the following scheme:
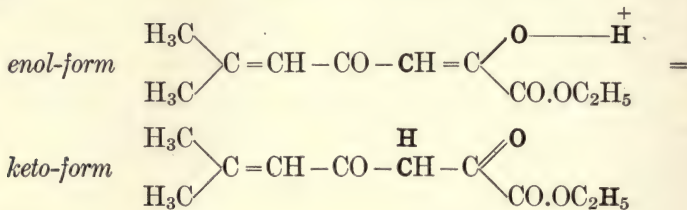
He says:

"The **C** atom of the unsaturated ethylenic group of the anion attracts the cation hydrogen, which loses its positive charge; at the same time, the hydroxylic oxygen of the anion loses its negative charge, and changes into the electrically neutral carbonylic oxygen."

Brühl's view, which, as he says, brings in no new hypothesis, regards the tautomerizing power of a solvent to be a measure of its ionizing power. One would expect the electric conductivity of the enolic form of ethylmesityloxidoxalate to be smallest in a freshly made solution in chloroform, larger in a solution in carbon bisulphide, benzene, or α-bromonaphthalene, and very much larger in alcoholic solutions. One would also expect the chloroform solution to retain its small conductivity for the longest time, the conductivity to decrease slowly in benzene, etc., solutions, and to decrease much more rapidly, until it disappears, in alcoholic solutions.

Brühl calls solutions of tautomerizable enolic compounds *conductors of the third order*. These electrolytic systems change continuously and more or less rapidly; whereas a conductor of the second order, that is, a solution of a salt, of an ordinary acid, or of a base, remains electrolytically constant, provided the concentration and the temperature are constant.

Brühl says:

"I regard the supplementary or residual affinity of certain atoms, especially of oxygen atoms, and particularly of those in hydroxylic groups— also of nitrogen atoms—to be the seat of the ionizing and tautomerizing power of media."

In attempting to find the cause of the varying activities of the solvents he examined, Brühl lays stress on the relativity

of the dissociating powers of solvents. A comparison of these powers, without reference to the particular substances dissociated, can only be qualitative. Speaking broadly, water dissociates compounds dissolved in it to a greater degree than organic media; alcohols are more complete dissociators than ketones; and so on. But, to take an example, although formic acid is an excellent dissociator of salts, yet some electrolytes—hydrogen chloride and trichloracetic acid, for instance—are not dissociated, but seem rather to be associated to double molecules, when dissolved in formic acid.[1] Hence a comparison of the dissociating powers of media with other properties of them can only be qualitative, can only be broad and general.

Nernst, in 1894, claimed to have established the existence of a connexion between the dissociating powers and the dielectric constants of solvents.[2]

Bodies which have great electric resistance "are called dielectrics, because certain electrical actions can be transmitted through them; . . . when an electromotive force acts on a dielectric it causes the electricity to be displaced within it in the direction of the electromotive force. . . . The amount of displacement produced by a given electromotive force is different in different dielectrics. The ratio of the displacement in any dielectric to the displacement in a vacuum due to the same electromotive force is called the Specific Inductive Capacity of the dielectric, or, more briefly, the Dielectric Constant." [3]

Brühl develops the connexion between the dielectric constants and the dissociating powers of solvents, premising that nothing beyond a broad and general connexion can be established, because comparisons of dissociating powers must be merely qualitative at present. All that can be regarded as established is, that liquids which have large dielectric constants and large dissociating powers are the best tautomerizors. It does not follow that a liquid which has the smallest dielectric constant of a series of liquid compounds is the slowest dissociator and tautomerizor.

What are the nature and conditions of the energy of solvents, called by Brühl the medial energy, by which the separation of

[1] See Zanninovich-Tessarin, *Zeitsch. für physikal. Chemie*, **19**, 251 [1896].

[2] *Zeitsch. für physikal. Chemie*, **13**, 531 [1894].

[3] Clerk Maxwell, *An Elementary Treatise on Electricity* (edited by W. Garnett), p. 108 [1881].

aggregates, the dielectric actions, and the processes of tautomerization and ionization, are accomplished?

The medial energy of a solvent depends on its chemical constitution. Although this form of energy cannot be identical with thermal energy (there are many instances of decrease of ionization accompanying increase of temperature), the two kinds of energy must be connected; for heating certain salts causes ionization of them, aggregates are simplified by solution and also by heat, tautomerization is accomplished by both of these forms of energy.

Brühl traces connexions between the medial energies and the heats of disgregation of solvents. If r equals heat of vaporization of a liquid compound, and ρ equals the heat of disgregation, or the disgregation-energy of the liquid, that is, the portion of the heat of vaporization which is used in overcoming intramolecular and intermolecular cohesion, then

$$r = \rho + A p (v - v_1),$$

where A is the thermal equivalent of unit work, $p =$ pressure, $v =$ volume of substance as a gas, and $v_1 =$ volume of substance as a liquid.

After tabulating and discussing the data available for determining the heats of disgregation of liquid compounds, under conditions such that the values are strictly comparable, Brühl comes to the conclusion that the crude heats of vaporization may be taken to be proportional to the heats of disgregation, provided only those compounds are considered which follow the gaseous laws, at least approximately, under the conditions whereat the heats of vaporization are determined.

Comparison of the heats of vaporization of about sixty solvents with their dielectric constants, so far as these constants have been determined, showed an undoubted connexion between the two series of values. Speaking broadly, good dissociators have large heats of vaporization and large dielectric constants; feeble dissociators have small heats of vaporization and small dielectric constants.

‘With the limitations already mentioned we may put the heats of vaporization of substances as proportional to their heat-content (*Wärmeinhalt*)

employed in internal work. Hence those solvents are characterized by the greatest dielectric capacity of separation (*Scheidungsvermögen*), and generally by the strongest medial energy, in the vaporization of which the greatest quantities of heat must be used for separating the liquid molecules, or molecular aggregates, and resolving them into single gas-molecules. When the heat of disgregation is small, the dielectric power of separation (*Scheidungskraft*) and the medial energy are generally small."

So far as determinations have been made of heats of fusion of substances used as solvents, it appears that the active dielectrics and dissociators have large heats of fusion, and feeble dielectrics and dissociators have small heats of fusion.

Although the specific heat of a substance is a complicated thermal property which cannot yet be exactly analyzed, yet it is possible to assert the existence of a correlation of specific heat and dissociating power. Active dissociators, as a class, have large specific heats; much medial energy generally accompanies high values of specific heat.

"Those solvents in which the forces of cohesion are strong, as shown by the heats of vaporization and of melting, and also, as a rule, by the specific heats, are characterized by considerable medial energy and capacity of association. A moderately large portion of the energy supplied in the form of heat to associated media must be used in disgregating molecular complexes; another portion will be employed in doing intramolecular work, in loosening atomic connexions. Under suitable conditions, therefore, the thermal capacities and the disgregation-energies, and hence the medial energies of non-associated solvents, may be considerable" [because little energy is needed to break up their molecular aggregates].

Brühl seems to think that the disgregation-energy of a solvent may be directly used for ionizing, or that the cohesion-energy of the liquid molecules may be transformed into ionizing energy. He says:

"The residual affinities of the media . . . appear to be the points of attack (*Angriffspunkte*) in those changes [of energy] which give rise to the formation of hydrates, ammonia compounds, and similar complex combinations of electrolyte and solvent, and, on sufficient accumulation of a suitable medium (dilution), lead to disruption of the electrolyte and to combination of the ionized portions with the dielectric, which is the solvent. In accordance with the views advanced, it is especially the oxygen and the nitrogen atoms of the solvent that are active; these atoms are not completely saturated by combination with two or with three univalent atoms . . . and contain supplementary or residual affinities."

Brühl claims that the establishment of a definite connexion between the medial energies and the thermal capacities of

solvents is the most practical result of the investigations described in his memoir on *the part played by the media in processes of solution*.[1]

Brühl and Schröder described the results of the further spectrometric study of certain tautomerizable systems in three memoirs published in 1904 and 1905, and showed that these results established an important connexion between spectrometry and electrochemistry, inasmuch as they yield an optical method for measuring the degrees of ionization of certain substances in solutions.[2]

So far as they have been examined, tautomerizable systems have more or less acidic or basic reactions: those of the aceto-acetic ester type form salts by interacting with certain bases; some amido- and imido-compounds are basic; many oxims are both acidic and basic, are *amphoteric* (ἀμφοτέρη, in both ways).

These tautomerizable substances have been called pseudo-acids and pseudo-bases, because the salts formed from them are desmotropic with regard to the parent compounds. It is to pseudo-acids and pseudo-bases that Brühl and Schröder devote their attention in the memoirs now to be considered.

The ketonic and the enolic forms of the sodium compounds of the esters of camphocarboxylic acid are formulated thus by Brühl and Schröder:

$$\text{(1) } \textit{keto-form} \quad C_8H_{14} \underset{\diagdown}{\overset{\diagup}{\vert}} \overset{\text{CNa.CO}_2\text{R}}{\underset{\text{C}=\text{O}}{}}$$

$$\text{(2) } \textit{enolic form} \quad C_8H_{14} \underset{\diagdown}{\overset{\diagup}{\Vert}} \overset{\text{C.CO}_2\text{R}}{\underset{\text{C.ONa}}{}}$$
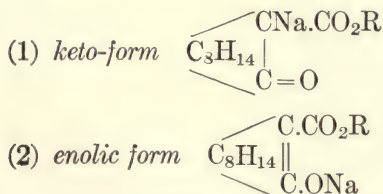
[1] For references to other memoirs on relations between the ionizing powers and the dielectric constants of solvents, see Mellor's "Chemical Statics and Dynamics," pp. 340–41. According to J. H. Mathews, no constant relation has been established between the ionizing powers and the dielectric constants of solvents. Mathews gives a very full bibliography of this subject (*J. phys. Chemistry*, **9**, 641 [1905]). But Walden's measurements of the dissociating powers of 49 solvents, on the same compound dissolved in them, show a close parallelism between the dissociating powers and the dielectric constants of the solvents (*Zeitsch. für physikal. Chemie*, **54**, 230 [1906].

[2] "Über Salzbildungen in Lösungen," *Zeitsch. für physikal. Chemie*, **50**, 1 [1904]; **51**, 1 [1905]; **51**, 514 [1905].

All the camphocarboxylic esters which have been examined are certainly keto-compounds. A solution of the sodium compound of one of the esters of camphocarboxylic acid in benzene, or other slightly dissociating solvent, does not react with alkyl haloid compounds; a solution of the same compound in alcohol, or other largely dissociating medium, interacts slowly but completely with alkyl haloid compounds to form keto-alkyl derivatives of the ester

$$C_8H_{14} \begin{cases} CR.'CO_2R \\ \\ C=O \end{cases}$$
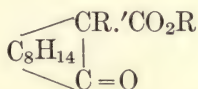
Acetyl haloid compounds react very readily with the sodium compounds of the esters in any solvent, and form only enol-derivatives [1]

$$C_8H_{14} \begin{cases} C.CO_2R \\ \| \\ C.OAc \end{cases}$$
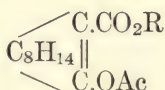
In order to elucidate these peculiar reactions, to determine the constitution of the ester salts of camphocarboxylic acid in solutions, Brühl and Schröder used three spectrometric methods. Sodium was dissolved in a definite quantity of absolute alcohol, and to this was added a definite quantity of the ester of camphocarboxylic acid. The alcohol, the sodium alcoholate solution, the ester, and the solution of the sodium salt of the ester were examined spectrometrically.

METHOD I.—*Determination of the spectrochemical function of the radical of the salt.* Solutions of the sodium-ester salts were regarded as mixtures of the ester and the sodium alcoholate solution. If the ester retains its original constitution when dissolved in alcoholic sodium alcoholate, that is, when the salt is formed, the molecular refraction and dispersion of the dissolved ester must be the same as the refraction and dispersion of the undissolved ester. If the ester changes its constitution when the salt is formed, the optical values of the dissolved ester must be greater than they were before solution, because of enolization.

---

[1] The esters of camphocarboxylic acid were examined in great detail by Brühl; the results are embodied in a series of memoirs in *Berichte,* **24, 26, 35, 36,** and **37** [1891 to 1904].

METHOD II.—*Determination of the spectrochemical function of the metal of the salt.* The spectrometric constants of the radical deducted from those of the salt give values for the dissolved metal. If the sodium in the ester-salt is in the combination NaOR, it will have the same optical constants as sodium in solutions of ordinary salts and of caustic soda (NaOH). But if the sodium is linked to carbon, is in the keto-compound, the constants will probably be markedly different from those of sodium in ordinary salts and in caustic soda.

METHOD III.—*"Spectrochemical differential method."* The ester-salt is formed by adding an alcoholic solution of sodium alcoholate to the ester. Let R be the radical which forms the ester by combining with hydrogen, and the ester-salt by combining with sodium; the formation of the salt is represented by the equation,

$$HR + C_nH_{2n+1}ONa = NaR + C_nH_{2n+1}OH. \quad . \quad . \quad (I)$$
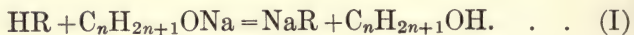
Let (M) be the optical function (molecular refraction or dispersion) of a member of this system; then

$$(M)NaR - (M)HR = (M)C_nH_{2n+1}ONa - (M)C_nH_{2n+1}OH = \varDelta$$
$$= constant \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (Ia)$$

The difference $\varDelta$ can depend only on the nature of the alcohol used and on the concentration. Now Brühl had already shown that optical function is an additive property only when the relations of atomic linkings are unchanged. If, therefore, the radical, R, of the ester is altered in the formation of the salt, we shall have, in place of (Ia), either

$$(M)NaR' - (M)HR < \varDelta \quad . \quad . \quad . \quad . \quad (Ib)$$

or
$$(M)NaR' - (M)HR > \varDelta \quad . \quad . \quad . \quad . \quad (Ic)$$

In his memoirs, *Die Rolle der Medien in Lösungsvorgangen,* and *Über tautomere Umwandlungen in Lösungen,* Brühl showed that all of these three possible cases sometimes actually occur.

If R remains constant, if no shifting of linkings happens in the process of solution of the ester in the alcoholic sodium alcoholate, equation (Ia) will hold good; if an enol-form

changes to a keto-form, in which case $(M)R' < (M)R$, expression (Ib) will be applicable; if a keto-form changes to an enol-form, the optical function of R' is greater than that of R, and expression (Ic) will be relevant.

In the cases considered (Ib) is excluded, for all camphocarboxylic esters are certainly keto-compounds; therefore, in the processes of solution, of salt-formation, the esters either remain keto-compounds, in which case R is constant, and (Ia) holds; or they are enolized, in which case $(M)R' > (M)R$ and (Ic) holds. Hence determinations of the values of Δ when different alcohols are used, and of the differences between the optical functions of sodium salts and the corresponding esters, will show whether the esters are unchanged, or are enolized, in the process of forming salts.

As the three methods severally control each other, the results are very trustworthy.

Brühl and Schröder determined the optical constants of three esters, the methyl, the ethyl, and the iso-amyl ester; of the three alcohols, methylic, ethylic, and amylic; of sodium methylate in methylic alcohol, sodium ethylate in ethylic alcohol, and sodium amylate in amylic alcohol; of the sodium salt of the methyl ester in methylic alcohol, the sodium salt of the ethyl ester in ethylic alcohol, and the sodium salt of the amylester in amylic alcohol. They determined the constants for various concentrations in each case. They say:

" In the solutions most concentrated as regards alcoholate, or as regards salt, the atomic refraction of sodium is almost absolutely unchanged in the three media and in the six sodium compounds. On the other hand, the atomic refractions of sodium are different in dilute solutions: the value is about 20 *per cent* larger in amylic alcohol solution than in solution in methylic or in ethylic alcohol; in these two alcohols the values are very nearly the same."

All the values were found to be always larger in concentrated solutions than in dilute solutions.

The most surprising result is the absolute identity of the optical function of sodium in the alcoholates and in the corresponding salts:

"For it follows from this that the alcoholates are ionized in dilute solutions in methylic and ethylic alcohol, and to the same extent as the salts, and that they, like the salts, are non-conductors in solutions in amylic alcohol."

The conclusion concerning the degree of ionization of the alcoholates and the salts in methylic and ethylic alcohols was confirmed by cryoscopic determinations, and by measurements of electric conductivities.

Brühl and Schröder found that the electric conductivities of sodium alcoholates in methylic, ethylic, and propylic alcohols had been determined in the laboratory at Amsterdam by Sijbe Tijmstra (under the direction of Lobry de Bruyn). As the conductivity of sodium methylate in methylic alcohol was found to be large, of sodium ethylate in ethylic alcohol to be smaller, and of sodium propylate in propylic alcohol to be much smaller, Brühl and Schröder concluded that the conductivity of sodium amylate in amylic alcohol will be found to be very small, probably almost *nil*.

These results led the authors to compare, with their determinations, the data obtained in measurements of the optical constants of sodium in solutions of caustic soda of varying concentration; to make a series of cryoscopic measurements with solutions of the sodium salts of camphocarboxylic esters in various solvents; and to supplement the data of other investigators regarding the electric conductivities of camphocarboxylic acid, its sodium salts and other derivatives, by a number of measurements made by themselves.

Bringing all their results into focus, Brühl and Schröder say:

"The simplest assumption, an assumption which completely explains the observations, is that the salts are not ionized in very concentrated solutions in methylic, ethylic, or amylic alcohol, are not ionized even in very dilute solutions in amylic alcohol, but are ionized in sufficiently dilute solutions in methylic and in ethylic alcohol.

"Inasmuch as the optical functions of sodium, of the ester-salts, and of the alcoholates vary to the same extent in solutions in methylic and in ethylic alcohol as concentration varies, it is probable that these two alcohols ionize the sodium compounds to approximately equal extents, and that the degree of ionization corresponds with the magnitude of the optical functions of the sodium; hence these functions will serve as direct expressions and measures of the state of dissociation."

The spectrometric function of sodium in dilute, and in concentrated aqueous solutions of caustic soda, was determined. Almost the same values were obtained for sodium ions in dilute

aqueous solution as in dilute methylic or ethylic alcoholic solution; and also the same values for non-ionized sodium, in very concentrated aqueous solution, as for non-ionized sodium in concentrated solutions of the ester-salts, and of the alcoholates in methylic, ethylic, or amylic alcohol. The optical values found for ionized sodium, in any of the solvents used, were from 12 to 15 *per cent* smaller than the optical values found for non-ionized sodium.

The peculiar chemical behaviours, towards different reagents, of the salts and ester-salts of camphocarboxylic acid in different solvents, inexplicable by the use of ordinary chemical methods of inquiry, are now explained. It is shown that the degree of association, or of ionization of the dissolved substance regulates the occurrence, or the non-occurrence of chemical transformations, and this state is dependent on the medial energy of the solvent used.

The work of Brühl proves indisputably the exceeding usefulness of the spectrometric method in both branches of chemical investigation. This method has done, and in the hands of Brühl is doing much to advance the examination of some of the finer problems of composition, and the elucidation of certain subtle aspects of chemical interactions. Moreover, the spectrometric method has succeeded where purely chemical methods have failed. That species of reversible isomeric change which is called tautomerism, or desmotropy, cannot be analyzed by those chemical methods which are used in examining the ordinary, one may say the coarser kinds of isomeric transformation; the spectrometric method has proved itself a delicate instrument for opening the door which admits to this room. And, in opening that door, this instrument has opened other doors also, through which light is falling into places that were dark before. Brühl's spectrochemical researches indicate a method for attacking questions of the connexions between the powers of solvents to make substances dissolved in them chemically active, and the other chemical and physical properties of these solvents.

Brühl's results open, or rather re-open, the question, Is chemical reactivity always associated with the presence of ions? (Compare the older question, Are the reactions of carbon com-

pounds the reactions of the radicals of these compounds? See Chapter IX, p. 241.)

In 1903, Walden gave a summary (with references to the original memoirs) of the researches which have extended the list of compounds that act as conductors of electricity, and are, therefore, more or less ionized.[1] He also cited the words of many chemists who have taught that chemical reactions are generally the reactions of ions, a view which found its fullest expression in the words of Arrhenius,[2] "One may even go so far as to assert that only ions can react chemically." Walden laid stress on the fact that many compounds which must be regarded as partially ionized cannot be included in the class of salts, and that, therefore, Hittorf's dictum,[3] "*all electrolytes are salts*," must be revised.

Walden made preliminary measurements of the conductivities of many substances in liquid sulphur dioxide, a compound which can scarcely be classed as a salt.[4] He then selected representatives of six groups of homogeneous substances, and made exact measurements of the conductivities of solutions of them in liquid sulphur dioxide, in arsenious chloride, in sulphuryl chloride, and, in some cases, in hydrazine hydrate, in aceto-nitrile, in acetic aldehyde, in ether, and in a few other solvents. The representative substances selected by Walden were these: the halogen elements bromine and iodine; the compounds iodine chloride and iodine bromide; the haloid compounds of phosphorus, arsenic, antimony, tin, and sulphur; certain tertiary nitrogen bases, also dimethyl pyrone, some carbinols, and some hydrocarbons; certain halogen compounds of hydrocarbons; some acid chlorides and bromides.

Walden very fully discussed his results for each group of substances examined. The most important general conclusion which followed from his determinations was, that "a great troop of chemical individuals which cannot be claimed to be salts,

---

[1] "Über abnorme Elektrolyte," *Zeitsch. für physikal. Chemie*, **43**, 385 [1903].

[2] *Lehrbuch der Elektrochemie*, p. 171 [1901].

[3] See Chapter XII, p. 329.

[4] Walden had found that liquid sulphur dioxide, arsenious chloride, phosphoryl chloride ($POCl_3$), thionyl chloride ($SOCl_2$), and sulphuryl chloride (SO_2Cl_2) are ionizing media.

acids, or bases, and cannot, therefore, be called electrolytes, nevertheless are often very good conductors of the electric current."

He then attempted to define the ions of these "abnormal electrolytes." As examples of his results, I give the following.

"The halogens (bromine and iodine), besides anions, furnish also *cations*, Br˙ and Br˙˙˙, and I˙ and I˙˙˙. The metalloids phosphorus, arsenic, antimony, tin, and sulphur are able to form *cations* also, and, indeed, P˙˙˙ and P˙˙˙˙˙, As˙˙˙, Sb˙˙˙ and Sb˙˙˙˙˙, Sn˙˙˙˙, S_2˙˙ " [1]

Walden concludes his memoir with these words:

"Consequently, we stand on a purely experimental basis as regards the ability of substances to form ions, and we dare not regard the facts concerning the electrolytic behaviour of substances which have been gained by examining aqueous solutions as exhaustive and typical for all solutions."

In communications made to the Chemical Society in 1904, Walker experimentally criticized the view that ionization always precedes chemical interaction.[2] He described parallel cases in only one of which interactions happened, although the conditions of both were exactly alike; for instance, a solution of dry hydrogen chloride in dry ether reacted with dry zinc, but a similar solution of trichloracetic acid did not react with dry zinc. In neither solution could ionization be detected.

Walker says that his experiments support the view that "ionization is dependent on chemical combination between solvent and dissolved substance, although it is by no means a necessary consequence of the latter." He attributes chemical combination with the solvent, in many cases at any rate, to the actions of the potential valencies of atoms of the substance which is dissolved.[3]

Reference has been made to the work of Perkin on the magnetic rotations of a class of carbon compounds. In Chapter XI (p. 308) the meaning was explained of the expression *optically active compounds*, and some account was given of the develop-

[1] The possible existence of anions and cations in the same elementary gas is provided for by the electronic theory (see Chapter XII, p 347). Walden's work is continued in *Zeitsch. für physikal. Chemie*, 46, 103 [1903].

[2] *C. S. Journal*, 85, 1082; 85, 1098 (with McIntosh and Archibald) [1904].

[3] Compare Abegg, *Zeitsch. für anorgan. Chemie*, 39, 330 [1904]. An account of this memoir is given in the *Chemical Society's Annual Reports on the Progress of Chemistry*, 1, 5 [1905]. For a résumé of recent results (to the latter part of 1905) on conductivity in non-aqueous solutions, see *Annual Reports, C. S.*, 1, 15; 2, 22.

ment of connexions between the constitutions of carbon com-
pounds and their ability to rotate the plane of polarization of a
ray of light.

By a series of measurements, extending over twenty years
(1882 to 1902), Perkin has thrown light on the relations between
the chemical compositions and constitutions of a vast number
of compounds and their powers of rotating the plane of polari-
zation when under magnetic influence.

The phenomenon of magnetic rotatory polarization was
discovered by Faraday [1] in 1845, and was studied chiefly by
him, by De la Rive [2] in 1868, and by Becquerel [3] in 1877. No
definite relations were established between this property and
the compositions of substances until Perkin began the syste-
matic study of this department of physical chemistry in 1882.[4]

If d is the relative density of a liquid compound, r the ob-
served rotation when it is placed between the poles of an electro-
magnet, and M is its molecular weight, then Perkin called the
value of

$$\frac{r.M}{d}$$

the *molecular rotatory power* of the compound, referred to water
as unity.

In a lengthy memoir, published in 1884, Perkin recorded
and discussed the molecular rotatory powers of about 140 car-
bon compounds, including hydrocarbons and their haloid
derivatives, aldehydes, acids, esters, and ethers.[5] He indicated
certain general connexions between the molecular rotatory
powers and the arrangements of the atoms in the molecules of
the compounds which he examined, and he gave formulæ for
calculating the rotatory powers of each of twenty-six series of
carbon compounds. Having found that the rotatory powers of
the constituent atoms of compounds are modified by the man-
ner of combination of these atoms, Perkin applied his results

[1] "On the magnetization of light and the illumination of the magnetic lines of
force," *Phil. Trans.* for 1846, pp. 1, 21, 61.
[2] *Annal. Chim. Phys.* [4], **15**, 57 [1868].
[3] *Ibid.* [5], **12**, 1 [1877].
[4] *C. S. Journal*, **41**, 330 [1882].
[5] *Ibid.*, **45**, 421 [1884]

to the elucidation of several chemical problems. In 1886 he attacked the question of "water of crystallization." [1] In 1889 he determined a series of values for nitrogen compounds, and also examined the effects of solvents on the rotatory powers of various compounds.[2] In 1892 and 1894 he dealt with the light thrown by the molecular rotatory powers of ketonic compounds on their constitutions, and made a study of certain cases of desmotropy.[3] The examination of unsaturated compounds [4] began in 1895; in 1896 appeared an exceedingly lengthy memoir, of more than two hundred pages, on aromatic compounds,[5] followed by another communication on the same subject [6] in 1902.

Perkin was not able to assign any definite values to the magnetic rotatory powers of the elementary atoms in the molecules of compounds. He considered the molecular rotatory powers of compounds to be conditioned not only by the nature and arrangement of the atoms in the molecules, but also by the molecular complexities of compounds, and by "the physical conditions induced by molecular arrangements."

The results of Perkin's laborious researches show that determinations of the magnetic rotatory powers of compounds have not furnished so discriminating an instrument for penetrating the very "joints and marrow" of chemical constitution as is given by the study of the refractive and dispersive powers of compounds.

Information regarding chemical composition and constitution has been gained by using the spectroscope to analyze the light from self-luminous substances, and the effects on rays of light of their passage through absorbing media.

The study of emission-spectra has led to the conclusion that each atom, when in the gaseous state, emits a definite set of light-waves. This study has also been the means of discovering

---

[1] *C. S. Journal,* **49**, 777 [1886]

[2] *Ibid.,* **55**, 680 [1889]

[3] *Ibid.,* **61**, 800 [1892]; **65**, 815 [1894].

[4] *Ibid.,* **67**, 255 [1895].

[5] *Ibid.,* **69**, 1025 [1896].

[6] *Ibid.,* **81**, 292 [1902]. No mention has been made in the text of several other memoirs by Perkin.

several elements, and has helped in the differentiation and the classification of elements and compounds.

The study of absorption-spectra has enabled certain general conclusions to be drawn regarding the absorptive powers and the chemical properties of classes of compounds, especially of carbon compounds, and has opened questions regarding the nature and relations of molecular and intramolecular vibrations. Descriptions of some of the results obtained by applying spectroscopic methods to problems of chemical constitution will be found in a book entitled *Spectroscopy*, by E. C. C. Baly [Longmans, 1905].

Section II.

Relations between changes of composition and thermal changes.

Every change of properties of a material system is accompanied by a change of energy. If the energy-change is reversed, if the original quantity and distribution of energy are restored, the properties of the system return to what they were before the cycle of changes began. An unelectrified system at rest, and at the same temperature and pressure as its surroundings, may contain energy which is removeable only by causing the system to change its composition. For example, when all the energy removeable without change of composition from a mixture of a gram of hydrogen and eight grams of oxygen has been removed, the system is still capable of doing a large amount of work. If electric sparks are passed through the mixture, the hydrogen and oxygen disappear, nine grams of water are formed, and a quantity of heat is produced which, if changed into mechanical work, would raise about 14,000 kilograms to the height of a metre.

The greater part of the energy which leaves the system $H_2 + O$, when it becomes H_2O leaves it in the form of heat, in which form it can be directly and easily measured. Measurements of the thermal values of definite changes of composition, and the interpretation of the results of these measurements, form the subject-matter of thermal chemistry.

Ostwald [1] notices two features of chemical energy which give it an especial importance in the economy of nature. It is an extremely lasting form of energy; a piece of coal may remain unchanged in its energy-content for many millenniums: and it is one of the most concentrated forms of energy; large quantities of chemical energy are easily carried from place to place condensed in comparatively small masses of changeable materials. Recent researches have shown that prodigious quantities of chemical energy are packed into exceedingly small spaces in the atoms of the radio-active elements, perhaps in the atoms of other elements also. Methods may some day be discovered for tapping these vast stores of concentrated energy.

The Memoirs of the French Academy of Sciences for the year 1780 contain a lengthy communication on heat by Lavoisier and Laplace. Another memoir on the same subject by the same naturalists was published after the death of Lavoisier.[2] In the first communication, the authors described a new method for measuring heat, experiments made by this method, and conclusions drawn from these experiments, and they considered the thermal phenomena attending combustion and respiration. In the second memoir, they described their attempts to render the method more accurate, and gave several determinations of heats of combustion, and of the specific heats of various substances.

The portions of these memoirs which are of the greatest import in the history of thermal chemistry are, the method for measuring the quantities of heat produced in processes of combustion, and the following generalization, deduced from a theory of heat, and to some extent confirmed by experiments:

"All thermal changes . . . exhibited by a system of bodies which changes its state repeat themselves in the opposite direction when the system returns to its original condition."

---

[1] *Lehrbuch der Allgemeinen Chemie*, vol. ii, p. 53.
[2] The whole of the first memoir and a full abstract of the second are given in the official collected edition of Lavoisier's *Œuvres*, vol. ii, pp. 283, 724. A German translation of these memoirs forms No. 40 of Ostwald's *Klassiker der exakten Wissenschaften*.

Ostwald [1] puts this general statement into the following more distinctly chemical form.

"The same quantity of heat is used in decomposing a compound into its constituents as is produced in the formation of the compound."

A series of "Thermochemical Investigations," by G. H. Hess, was published in the years 1839–1842 in the *Bulletin scientifique, publié par l'Académie Impériale des Sciences de St. Pétersbourg.* German translations of these memoirs (probably by Hess himself) appeared simultaneously in *Poggendorff's Annalen der Physik und Chemie.* No. 9 of Ostwald's *Klassiker der exakten Wissenschaften* contains the German translation of Hess' memoirs, with notes by Ostwald.

Hess laid the foundations of thermal chemistry. He was the first to make a systematic study of the thermal values of chemical processes, and to enunciate the regularities which hold good in thermochemical changes.

In his earlier memoirs, Hess endeavoured to establish experimentally the following proposition, which we now know to be incorrect.

"When two substances combine in several proportions, the quantities of heat which are produced in the formation of the different compounds stand to one another in multiple proportions."

The next generalization made by Hess forms the basis of all indirect thermochemical measurements.

"The quantity of heat produced in the formation of a compound is constant, whether the compound is formed directly or indirectly."

Hess based this generalization on experimental results obtained in his thermal examination of the neutralization of acids by bases. He measured the heat produced by neutralizing a concentrated acid by a dilute aqueous solution of a base; he then added a determinate quantity of water to the concentrated acid, measured the heat produced, neutralized the solution of the base by this diluted acid, and measured the thermal value of the neutralization. He found that the thermal value of the total reaction was equal to the sum of the values of the partial reactions. I give some of Hess' data.

---

[1] *Lehrbuch,* ii, p. 54.

I.

| Composition of acid. | Quantity of heat produced | | Sum of heats. |
	By neutralization with ammonia.	By dilution with water.	
$H_2O.SO_3$	595·8		595·8
$2H_2O.SO_3$	518·9	77·8	596·7
$3H_2O.SO_3$	480·5	116·7	597·2
$6H_2O.SO_3$	446·2	155·6	601·8
			Mean 597·9

| Composition of acid. | Quantity of heat produced | | Sum of heats. |
	By neutralization with potash.	By dilution with water.	
$H_2O.SO_3$	597·2		597·2
$2H_2O.SO_3$	527·1	77·8	604·9
$3H_2O.SO_3$	483·4	116·7	600·1
$6H_2O.SO_3$	443·4	155·6	599·0
			Mean 600·2

Similar experiments were conducted with soda, and with lime; with hydrochloric acid and the four bases, ammonia, potash, soda, and lime; and with nitric acid and the same four bases. The results of these experiments were collected by Hess in the following table.[1]

II.

	$H_2O.SO_3$	$8H_2O.N_2O_5$	$12H_2O.H_2Cl_2$
KO Aq	601	409	361
NaO Aq	605	410	368
N_2H_6Aq	598	404	368
CaO Aq	642	451	436

From these data Hess concluded that the heats of neutralization of the four bases by the same acid are equal, and that the proportion between the heats of neutralization of a base by the three acids is the same for the four bases. Hence, Hess

[1] Hess used the Berzelian notation, wherein barred letters represent double atoms, and atoms of oxygen are represented by dots; thus, $\overline{H}^{..} = 8H_2O$, K Aq = KO Aq. He took the atomic weight of potassium as 78, and that of sodium as 46.

said, it is only necessary to know the heat produced by the neutralization of any one of the acids by any one of the bases, in order to determine the quantity of heat produced by the action of that base with the other acids, or of that acid with the other bases. Hess attributed the abnormally high results obtained with lime to the heat produced during the gradual combination with water of calcium sulphate, nitrate, and chloride. Hess did not venture to apply his generalization absolutely to all acids and bases; he thought that the values might vary in different groups of acids or of bases. Investigations made in recent years have shown that the heat of neutralization of a strong acid by any strong base is a constant quantity.

The next step made by Hess was the announcement of the *law of thermoneutrality.*

"Another phenomenon now demands our attention. Taking two solutions of neutral salts which have the same temperature and produce two new salts by double decomposition, the temperature does not change; another time the change of temperature is scarcely noticeable; so that neutral, intermingled solutions are *thermoneutral.*"

The law of thermoneutrality was regarded by Hess as contained in the table given on p. 505 (Table II). He selected the following data from that table.

$$
\begin{array}{llr}
\text{For CaO} & N_2O_5 & 451 \\
\text{For KO} & SO_3 & 601 \\
\hline
& \text{Sum} & 1052
\end{array}
$$

After mixing, one has

$$
\begin{array}{llr}
\text{For CaO} & SO_3 + H_2O & 642 \\
\text{For} & KO \quad N_2O_5 & 409 \\
\hline
& \text{Sum} & 1051
\end{array}
$$

In some cases there did not appear to be exact thermoneutrality. For example:

$$
\begin{array}{rl}
CaCl_2Aq = & 436 \\
KOSO_3Aq = & 601 \\
\hline
& 1037
\end{array}
\qquad \text{and} \qquad
\begin{array}{rl}
CaOSO_3Aq = & 642 \\
KCl\ Aq = & 361 \\
\hline
& 1003
\end{array}
$$

The reason of this difference, Hess said, is clear.

"More water was combined before than after the experiment; and thermoneutrality is complete only when all the conditions are the same, that is, when two salts free from water produce two equally waterless salts, or when the quantity of water combined in one case is the same as that in the other case."

Investigations made of late years have confirmed Hess' law of thermoneutrality.

The main portion of Hess' *thermochemical investigations* is devoted to the examination of certain chemical problems connected with the reactions of acids and the constitutions of salts. Hess applied thermal methods to elucidate the state of an acid in aqueous solution, the mechanism of the reactions between acids and bases and between metals and acids, the constitutions of acids—whether they are compounds of radicals with water or compounds of hydrogen, the connexions between thermal and electrical phenomena, and other similar questions. In order to find the thermal values of partial reactions which form inseparable portions of more complete changes, Hess frequently made use of his principle (*Das Princip der Beständigkeit der Summen*), that the heat produced in a chemical change is always the same, whether the change proceed all at once, or in any number of separate steps.

The work of Hess was conducted on the same lines as that of the later thermochemical investigators; his methods were similar to those which they have employed. In his *Lehrbuch* (ii, p. 57) Ostwald says:

"In this work, marked by genius, we see an adumbration of the whole development of modern thermal chemistry; later investigation had but to carry out the programme which was indicated here."

And the work of Hess is also marked by the same boldness of speculation, and the same trust in the conclusions drawn from the application of thermal methods to chemical problems as are to be found in the work of the later masters in this branch of physical chemistry. Thermal chemistry never grows old; it is always self-satisfied, always infallible.

How has the subject which Hess opened been gone into? I will not do more than trace the outlines of a very few of the more important advances which have been made in thermal chemistry. I say nothing about the details of the multiform applications of the fact that the total heat of a reaction is independent of the stages into which the reaction may be divided. This proposition follows from the principles of energy; but it should be remembered that it was enunciated by Hess as an empirical generalization from experimentally established facts before the theory of energy had been placed on a firm basis by the researches of Joule and of Helmholtz. I do not think it is necessary to describe the methods used for measuring the quantities of heat produced in chemical changes, nor to enter into an historical criticism of these methods. A discussion of the accuracy of the calorimetric methods for determining the heats of combustion of carbon compounds, conducted by Thomsen, Berthelot, and D. Lagerlöf, will be found in the pages of *Zeitsch. für physikal. Chemie*, and *Compt. rendus*, for 1905.

The quantities of heat produced in chemical changes are stated in calories. One gram-calorie is sometimes defined to be the quantity of heat required to raise the temperature of one gram of water from 0° to 1°, sometimes as the hundredth part of the heat given out by one gram of water in cooling from 100° to 0°. In actual practice the gram-calorie is the quantity of heat required to raise the temperature of one gram of water through 1°, at about 18°. The gram-calorie is usually represented by the abbreviation *cal*. Berthelot employs a unit equal to 1000 gram-calories; it is respresented by *Cal*. Some recent workers in thermal chemistry, following Ostwald, use as unit the quantity of heat given out by one gram of water in cooling from 100° to 0°, and represent it by the letter K.

In his more recent writings, Ostwald states the thermal values of chemical changes in units of work. The unit of work, one *erg*, is the work done in accelerating the motion of a mass weighing one gram by one centimetre per second. If the quantity of heat represented by one gram-calorie is transformed into mechanical work, it is found to be equal to 41,830,000 ergs. In technical measurements it is customary to designate ten

million ergs by the name one *joule*.   Ostwald uses one thousand joules = one Joule as his unit of work.[1]

Andrews and Graham should be mentioned as among those who helped to establish thermal chemistry. Their investigations appeared in the *Philosophical Transactions* from 1845 to 1848. In 1852 and 1853 several important memoirs by Favre and Silbermann were published in *Annales de Chimie et Physique*.

In the front rank of thermochemical inves gators since the time of Hess are to be placed Berthelot and Thomsen. Berthelot's *Essai de Mécanique Chimique fondée sur la Thermochimie* was published in 1879 (two vols.); and Thomsen's *Thermochemische Untersuchungen* appeared in the years 1882 to 1886 (four vols.).[2]   Among other investigations in thermal chemistry, a prominent place must be given to a long series of researches on the heats of reaction of carbon compounds by F. Stohmann, published from 1885 onwards in *Journal für praktische Chemie*. In 1890 and 1892 Stohmann collected and arranged most of the data which had been obtained by himself and by other investigators regarding the heats of combustion of organic compounds.[3]   Since that time Stohmann has continued his measurements of the heats of combustion of compounds of carbon, publishing his results in *J. für prakt. Chemie*.

The first volume of Thomsen's *Thermochemische Untersuchungen* is concerned with the thermochemical aspects of the neutralization of acids and of bases. The second volume is devoted to a thermochemical investigation of the reactions of compounds of nonmetallic elements, and the classification of the affinity-phenomena of these elements. The third volume deals with the thermochemical phenomena presented by dissolution in water, and hydration, and with the affinity-phenomena of metals. The fourth volume contains a thermochemical investigation of carbon compounds.

---

[1] One cal. = 41,830,000 ergs = 4·183 joules = ·004183 Joule.
   One Cal. = 41,830,000,000 ergs = 4183 joules = 4·183 Joules.
   One K = 4,183,000,000 ergs = 418·3 joules = ·4183 Joule.
   One joule = ·2391 cal. = ·0002391 Cal. = ·002391 K.
   One Joule = 239·1 cal. = ·2391 Cal. = 2·391 K.

[2] In 1905 Thomsen published a résumé of his chief experimental results and theoretical discussions, in one volume, entitled *Systematisk Gennemførte Termokemiske undersøgelsers numeriske od teoretiske Resultater.*

[3] *Zeitsch. für physikal. Chemie*, 6, 334 [1890]; 10, 410 [1892].

I will give a brief sketch of some of the more general results of Thomsen's thermochemical examination of the neutralization of acids and of bases.

The *heat of neutralization* of an acid by a base, or of a base by an acid, is the quantity of heat which is produced when equivalent weights of the two compounds interact, in dilute aqueous solution, to form a normal salt which remains in solution. Thomsen used gram-equivalent weights and expressed the thermal reactions in gram-calories.

Thomsen's results led him to arrange the commoner acids in four groups. The following approximately constant values were obtained for the heats of neutralization of the acids in each group. In the first group, 10,000 cals.; in the second group, 12,500 cals.; in the third group, 13,500 cals.; and in the fourth group a number ranging from 14,000 to 16,000 cals.

Thomsen divided the bases into two groups. In the first group he placed the hydroxides, and assigned the mean value of 15,650 cals. to their heat of neutralization; in the second group he placed ammonia and the amines, giving the mean value of 14,000 cals. to the heat of neutralization of a base in this group.

Hess supposed that the heats of neutralization of acids are independent of the nature of the base which is used. Andrews thought that the quantity of heat produced in the neutralization of an acid is dependent only on the nature of the base which is employed. Favre and Silbermann put the law of thermo-neutrality into its proper form by stating that the differences between the heats of neutralization of any two acids by any base have a constant value, and the differences between the heats of neutralization of any two bases by any acid are constant. Let the compositions of various salts be represented by the following scheme.

$$A+B \qquad A'+B \qquad A''+B \qquad A'''+B \ \ldots$$
$$A+B' \qquad A'+B' \qquad A''+B' \qquad A'''+B' \ldots$$
$$A+B'' \qquad A'+B'' \qquad A''+B'' \qquad A'''+B''\ldots$$

Let $f(A+B)$, $f(A'+B)$, $f(A''+B)$, etc., represent the thermal values of the neutralizations of the acid A by the base B, of

the acid A′ by the base B, of the acid A″ by the base B, and son on. Then the law of thermoneutrality asserts that

$$f(A+B) + f(A'+B') - f(A+B') - f(A'+B) = 0;$$
or $\quad f(A+B) - f(A+B') = f(A'+B) - f(A'+B'),$
and $\quad f(A+B) - f(A'+B) = f(A+B') - f(A'+B').$

. . . .

The law of thermoneutrality has been found to hold good in all normal reactions between acids and bases, provided that very dilute aqueous solutions are employed. The law asserts that, in the normal formation of a salt by the reaction of very dilute aqueous solutions of an acid and a base, the acid contributes a definite portion of the total heat of neutralization independently of the nature of the base, and the base contributes a definite portion of the total heat of neutralization independently of the nature of the acid. In other words, the law of thermoneutrality asserts that the individual character of the salt which is formed in a process of neutralization is without effect on the thermal value of that process.

The following is a translation of part of Ostwald's analysis of the law of thermoneutrality.[1] Considering the heat of neutralization of an acid by a base, represented by the expression $f(a,b)$, Ostwald says:

"The magnitudes $f(a,b)$ must be of the form

$$f(a,b) = \phi(a) + \phi(b) + c;$$

that is, the heat of neutralization is the sum of an individual energy-change of the acid $\phi(a)$, *plus* an individual energy-change of the base $\psi(b)$, *plus* a constant c, which must have the same value for all salts. The two magnitudes $\phi(a)$ and $\psi(b)$ are completely independent of one another. . . . If we consider the scheme of the formation of a salt from an acid and a base, the formation of sodium chloride for instance,

$$HCl + NaOH = NaCl + H_2O,$$
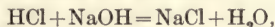
we see that it proceeds as follows: the acid loses its hydrogen, the base its hydroxyl; the acid-residue and the metal combine to form the salt, hydrogen and hydroxyl to form water. The corresponding total change of energy, the heat of neutralization, N, consists, therefore, of the following parts:

> change of the acid $\phi(a)$,
> change of the base $\psi(b)$,
> formation of water c,
> formation of salt $\chi(a,b)$;
> $N = \phi(a) + \psi(b) + \chi(a,b) + c.$

---

[1] *Lehrbuch*, ii, pp. 181, 182.

Now, it follows, from the law of Hess, that the heat of neutralization, N, contains the terms

$$N = \phi(a) + \phi(b) + c.$$

That the foregoing statement should be in keeping with experience, it is necessary that

$$\chi(a,b) = 0;$$

that is, the reaction of the acid-residue and the metal produces no change of energy. This means nothing more than that the two are independent and do not reciprocally influence one another. . . ."

When these facts concerning the heats of neutralization of acids and bases, in dilute aqueous solutions, are translated into the language of the ionic hypothesis, they tell that the formation of the salt is not accompanied by any change of the energies of its ions, that the ions exist side by side in the solution of the salt with unchanged energy-content, and, therefore, with unchanged properties.[1]

The history of the investigation of the *strengths* of acids and bases was sketched in Chapter XIV. We found that the ionic presentation of the strengths of these classes of compounds has been adopted by most chemists as an admirable working hypothesis, and that a *strong* acid, or a *strong* base, is described as an acid, or a base, which in dilute aqueous solution is dissociated to a very large extent into its ions. The law of thermoneutrality when interpreted by the ionic hypothesis, represents the neutralization of a strong monobasic acid by a strong mono-acid base, both in dilute aqueous solution, by the following scheme:

$$\dot{H} + \dot{R} + \dot{M} + O\dot{H} = \dot{M} + \dot{R} + H_2O.$$
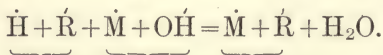
From this it follows that the heat of neutralization of a dilute aqueous solution of a strong acid by a dilute aqueous solution of a strong base is a constant quantity. Thomsen's data indicate that the constant value is about 14,000 cals. From a consideration of many results, Arrhenius, in 1889, concluded that the true value of the constant is very nearly 13,600 cals.[2]

According to the ionic hypothesis, this number expresses the heat of formation of electrically neutral water from its ions, from hydrion and hydroxidion.

---

[1] Compare Ostwald, *Lehrbuch*, ii, p. 182.
[2] *Zeitsch. für physikal. Chemie*, **4**, 107 [1889].

Attempts have been made to explain the constancy of the heat of neutralization of strong acids by strong bases without using the hypothesis of electrolytic dissociation.[1]

Thomsen's results proved that the heats of neutralization of all acids are not the same. How are such values as 10,000 or 11,000 cals. to be accounted for? The ionic hypothesis says that a dilute aqueous solution of a *weak* acid, or of a *weak* base, contains many un-ionized particles of the acid, or of the base, besides the ions of the acid, or the ions of the base. If the acid were altogether un-ionized, the neutralization of it by caustic soda would be expressed thus:

$$HR + \overset{.}{Na} + O\overset{'}{H} = \overset{.}{Na} + \overset{'}{R} + H_2O,$$
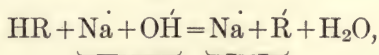
and the thermal reaction would be (1) separation of the acid into its ions, and (2) combination of hydrion (from the acid) with hydroxidion (from the base) to form water. The heat of neutralization of the acid would be greater or less than the value for a strong acid, namely 13,600 cals., according as heat was produced or used in the ionization of the acid. The most general case is that the acid is partially ionized. Ostwald[2] considers this case. He expresses the process of neutralization by the scheme

$$x\overset{.}{H} + x\overset{'}{R} + (1-x)HR + \overset{.}{Na} + O\overset{'}{H} = \overset{.}{Na} + \overset{'}{R} + H_2O,$$
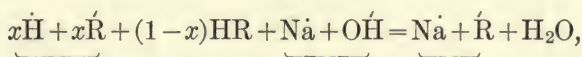
and the heat of neutralization by the statement,

$$N = 13,600 + (1-x)d_a,$$

where d_a is the heat of ionization of the acid.

"Entirely similar considerations hold good for the bases. Putting d_b as the heat of dissociation of any base, the neutralization of such a base by any acid will give the heat of neutralization

$$N = 13,600 + (1-x)d_a + (1-y)d_b,$$

where y is the dissociated portion of the base. Comparing this result with that deduced from the law of thermoneutrality [p. 511], we find them onformable, since

$$\phi(a) = (1-x)d_a, \quad \psi(b) = (1-y)d_b,$$

and c is to be taken as 13,600 cals."

---

[1] For example, by H. Crompton, *C. S. Journal*, **71**, 951 [1897].
[2] *Lehrbuch*, ii, pp. 203, 204.

Ostwald (l.c.) shows that the law of thermoneutrality is a necessary consequence of the ionic hypothesis and the empirical fact that the degrees of dissociation of analogous neutral salts are approximately equal (nearly complete). If the salts are not equally dissociated, the law of thermoneutrality cannot hold good.

Thomsen showed that the heats of neutralization of some dibasic acids are divisible into two equal portions, according as one or two equivalent weights of caustic soda are allowed to react with one formula-weight of the acid; and that with some dibasic acids the thermal value of each stage of the total operation is different. He gave the following examples.

$$H_2SiF_6 \text{ Aq} + NaOH \text{ Aq} = 13{,}300 \text{ cals.} \qquad H_2SiF_6 \text{ Aq} + 2NaOH \text{ Aq}$$
$$= 2 \times 13{,}300 \text{ cals.}$$

$$H_2SO_3 \text{ Aq} + NaOH \text{ Aq} = 15{,}850 \text{ cals.} \qquad H_2SO_3 \text{ Aq} + 2NaOH \text{ Aq}$$
$$= (2 \times 15{,}850) - 2750 \text{ cals.}$$
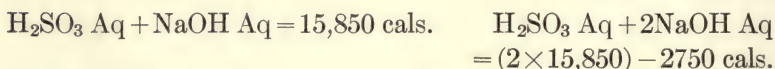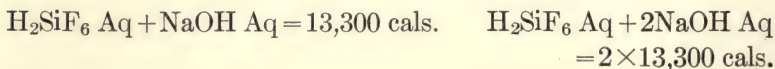
Similar results were obtained with tribasic acids. In some cases the heat of neutralization was divisible into three (approximately) equal portions; in some cases the thermal value of each equivalent weight of soda was different from that of the other equivalent weights of soda. For example, these are Thomsen's data for citric acid and for arsenic acid:

$$H_3C_6H_5O_7 \text{ Aq} + xNaOH \text{ Aq.} \qquad H_3AsO_4 \text{ Aq} + xNaOH \text{ Aq.}$$
$$x = 1 = 12{,}650 \text{ cals.} \qquad\qquad x = 1 = 15{,}000 \text{ cals.}$$
$$x = 2 = (2 \times 12{,}650) + \ \ 150 \text{ cals.} \qquad x = 2 = (2 \times 15{,}000) - 2400 \text{ cals.}$$
$$x = 3 = (3 \times 12{,}650) + 1050 \text{ cals.} \qquad x = 3 = (3 \times 15{,}000) - 9050 \text{ cals.}$$
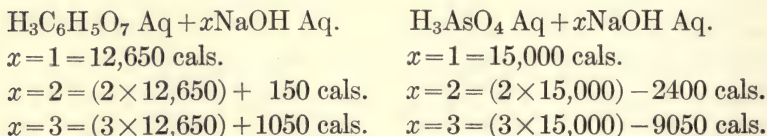
Thomsen suggested the following typical formulæ.

Dibasic Acids.

Typical formula	RH_2		Example	SiF_6H_2
" "	$R(OH)_2$		"	$SO_2(OH)_2$
" "	$R(OH)H$		"	$SO_2(OH)H.$

Tribasic Acids.

Typical formula	$R(OH)_3$		Example	$C_6H_5O_4(OH)_3$
" "	$HR(OH)H$		"	$HAsO_3(OH)H.$

Thomsen considered the bearing of his results on questions concerned with the constitutions of the acids which he examined thermochemically. As an example of his method and conclusions, I refer the reader to his treatment of periodic acid.[1]

Ostwald has analyzed the thermochemical phenomena presented by the neutralization of dibasic acids from the position of the hypothesis of ionization.[2]

If the dibasic acid (H_2R_{11}) is assumed to be completely ionized, the process of neutralization will be represented by the scheme

$$\dot{H} + \dot{H} + R_{11} + 2\dot{Na} + 2O\dot{H} = \dot{Na} + \dot{Na} + \ddot{R}_{11} + 2H_2O.$$
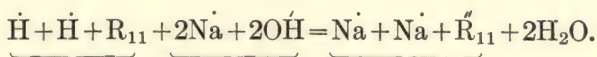
The heat of neutralization, that is, the heat of formation of $2H_2O$ from its ions, will be $13,600 \times 2 = 27,200$ cals. If the normal salt is added to the free acid, the reaction will be

$$\dot{H} + \dot{H} + \ddot{R}_{11} + \dot{Na} + \dot{Na} + \ddot{R}_{11} = 2(\dot{H} + \dot{Na} + \ddot{R}_{11}).$$
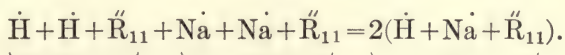
There will be no thermal change. Those dibasic acids to which Thomsen gives the typical formula RH_2 belong to this class; their neutralization-phenomena are completely comparable with those of the strongest monobasic acids.

If the dibasic acid (H_2R_{11}) is assumed to be completely un-ionized, the steps in the process of neutralization will be these:

(i) $H_2R_{11} + \dot{Na} + O\dot{H} = H\dot{R}_{11} + \dot{Na} + H_2O,$

(ii) $H\dot{R}_{11} + \dot{Na} + \dot{Na} + O\dot{H} = \ddot{R}_{11} + \dot{Na} + \dot{Na} + H_2O.$
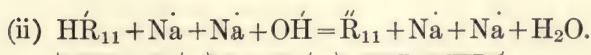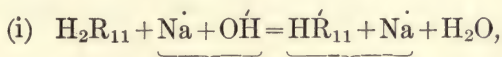
The thermal change in (i) will be composed of the heat of formation of H_2O from its ions (13,600 cals.), and the heat of ionization of the first atom of hydrogen $= d_1(H_2R_{11} = \dot{H} + H\dot{R}_{11})$. The thermal change in (ii) will be $13,600 + d_2$ cals., where d_2 is

---

[1] *Thermochemische Untersuchungen*, vol. i, p. 244, and onwards
[2] *Lehrbuch*, vol. ii, pp. 206-208.

the heat of ionization of the second atom of hydrogen of the acid ($H\dot{R}_{11} = \dot{H} + \ddot{R}_{11}$). In most cases, d_1 will not be the same as d_2, and the thermal values of the two equivalent weights of soda will differ. Finally, if the free, un-ionized acid is mixed with the normal salt, we have the scheme

$$H_2R_{11} + \underbrace{\dot{N}a + \dot{N}a + \ddot{R}_{11}} = \underbrace{H\dot{R}_{11} + H\dot{R}_{11} + \dot{N}a + \dot{N}a.}$$
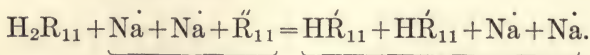
The accompanying thermal change will be $d_1 - d_2$; that is to say, it will be equal to the difference between the heats of neutralization of the first and second equivalents of soda, for these heats are severally $13,600 + d_1$ cals., and $13,600 + d_2$ cals., and the difference between these is $d_1 - d_2$. Inasmuch as the condition $2H\dot{R}_{11}$ is generally much more stable than the condition $\ddot{R}_{11} + H_2R_{11}$, the former will tend to be produced whenever it is possible.

Ostwald then analyzes the most general case, which is that of partial ionization of the dibasic acid.[1] The account I have given of his analysis of the two limiting cases—complete ionization and no ionization—will suffice to indicate his method of procedure.

I will now give a brief summary of Thomsen's thermochemical method of attacking this problem: When two acids and one base react in equivalent quantities in dilute aqueous solution, and all the products of the reaction are soluble in water, in what proportion does the base distribute itself between the two acids?

Using sulphuric acid, nitric acid, and caustic soda, it is evident that the system will attain equilibrium when it is composed of certain quantities of the four compounds, sodium sulphate, sodium nitrate, sulphuric acid, and nitric acid; and that the same distribution of these compounds will accompany the attainment of equilibrium whether the reaction starts with equivalent quantities of the two acids and soda, or with equivalent quantities of one of the acids and the normal sodium salt

---

[1] *Lehrbuch,* vol. ii, pp. 207, 208.

of the other acid. The distribution of the compounds before and after the reaction may be thus expressed:

$$\mathrm{Na_2SO_4\,Aq + H_2N_2O_6Aq} = x\mathrm{Na_2N_2O_6Aq} + x\mathrm{H_2SO_4Aq} \\ + (1-x)\mathrm{Na_2SO_4Aq} + (1-x)\mathrm{H_2N_2O_6Aq}.$$
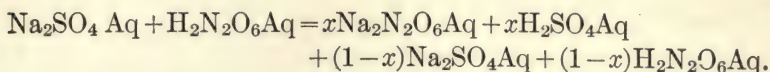
The total thermal change may be analyzed and represented by the following scheme.

$$\mathrm{Na_2SO_4Aq + H_2N_2O_6Aq} = x[\mathrm{H_2N_2O_6Aq + Na_2O_2H_2Aq}] \\ - x[\mathrm{H_2SO_4Aq + Na_2O_2H_2Aq}] \\ + [(1-x)\mathrm{Na_2SO_4Aq} + x\mathrm{H_2SO_4Aq}] + [x\mathrm{Na_2N_2O_6Aq} \\ + (1-x)\mathrm{H_2N_2O_6Aq}] \\ + [(1-x)\mathrm{H_2N_2O_6Aq} + x\mathrm{H_2SO_4Aq}].$$
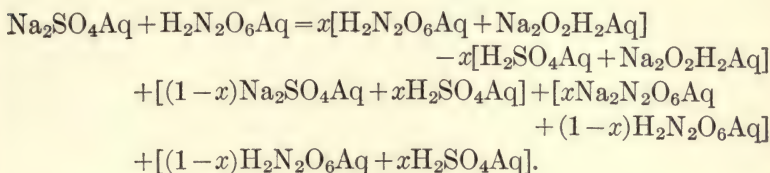
Thomsen measured the thermal value of each portion of the change, and the value of the total change. The observed value of the total change was -3504 cals. Omitting those portions which were found to have very small thermal values, and putting the reaction into a more convenient form, Thomsen gave the following statement.

$$\mathrm{Na_2SO_4Aq + H_2N_2O_6Aq} = x([\mathrm{H_2N_2O_6Aq + Na_2O_2H_2Aq}] \\ - [\mathrm{H_2SO_4Aq + Na_2O_2H_2Aq}]) \\ + (1-x)[\mathrm{Na_2SO_4Aq} + \frac{x}{1-x}\mathrm{H_2SO_4Aq}] = -3504 \ \text{cals.}$$
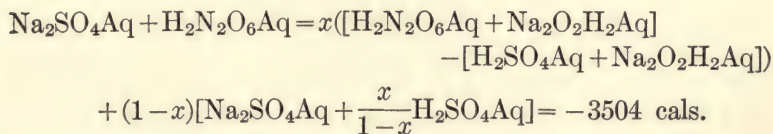
Substituting Thomsen's observed thermal values, we have

$$\mathrm{Na_2SO_4Aq + H_2N_2O_6Aq} \\ = x \times -4144 + (1-x)[\mathrm{Na_2SO_4Aq} + \frac{x}{1-x}\mathrm{H_2SO_4Aq}] \\ = -3504 \ \text{cals.}$$
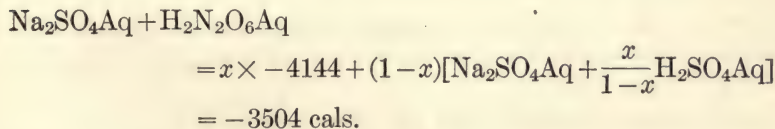
Thomsen took $x = \frac{2}{3}$, and calculated the thermal value of the reaction as follows.

$$\mathrm{Na_2SO_4Aq + H_2N_2O_6Aq} = \frac{2}{3} \times -4144 + \frac{1}{3}[\mathrm{Na_2SO_4Aq + 2H_2SO_4Aq}] \\ = \frac{2}{3} \times -4144 + (\frac{1}{3} \times -2352) \\ = -3546 \ \text{cals.}$$
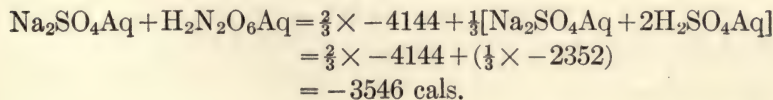
The thermal value of the reverse action was calculated from the equation:

$$Na_2N_2O_6Aq + H_2SO_4Aq$$
$$= (1-x)4144 + (1-x)[Na_2SO_4Aq + \frac{x}{1-x}H_2SO_4Aq].$$

Putting $x = \frac{2}{3}$, we have

$$= \frac{1}{3} \times 4114 + (\frac{1}{3} \times -2352)$$
$$= 597 \text{ cals.}$$

The observed thermal value of the reverse reaction was 576 cals.

Thomsen drew the following conclusions from the results of this investigation. When equivalent quantities of soda, nitric acid, and sulphuric acid react in dilute aqueous solution, two thirds of the soda combine with the nitric acid, and one third combines with the sulphuric acid. The striving of the nitric acid to saturate itself with the base, called by Thomsen the *avidity* of that acid, is twice as great as the avidity of the sulphuric acid. The expression *strength* of an acid is now generally used in place of Thomsen's term *avidity* of an acid.

Passing over Thomsen's thermochemical investigation of solution and hydration, and of the classification of elements, let us glance at one or two of the results of his examination of carbon compounds. The character and scope of Thomsen's conclusions will be evident from the following generalizations which I quote from Vol. IV of his *Untersuchungen*.

"In a series of homologous carbon compounds, the heat of combustion increases from member to member by an almost constant quantity, the mean value of which is 157,870 cals."

From this it follows that the atomic group CH_2 always performs a similar function in homologous carbon compounds, for CH_2 is the common difference between the composition of successive members of an homologous series:

"The heat of formation of a molecule of a carbon compound proves itself to be the sum of the thermal values of the individual atomic linkings. . . . The heat of formation of the molecule is dependent on the nature of the atomic linkings."

"The four valencies of the carbon atom have equal [thermal] values."

"The quantities of heat which correspond to a single and a double linking between two carbon atoms are almost equal, and vary from 14,000 to 15,000 cals., according to the nature of the compounds. The thermal value of a treble linking is equal to zero."

"The heats of formation and the heats of combustion of isomeric hydrocarbons differ only when the isomerides contain different numbers of single or double linkings between the atoms of carbon."

"The heats of formation and the heats of combustion of all hydrocarbons whose constitutions are known can be calculated by general formulæ."

"The heat of formation of a hydrocarbon depends on the number of hydrogen atoms, the number of carbon atoms, and the single and double linkings between the latter; the influence of treble linkings is equal to zero. For example, the formation of the compound $C_a H_{2b}$, from amorphous carbon and molecular hydrogen, will produce a quantity of heat which can be calculated by the formula

$$C_a + H_{2b} = b \times 30,000 + n \times 14,200 - a \times 38,380 \text{ cals.,}$$

where n denotes the sum of the single and double linkings, and the heat of formation is calculated for the compound in the state of gas at 18° and constant volume."

"Aromatic compounds contain no double linkings in the benzene nucleus. The six carbon atoms of the nucleus are held together by nine single linkings."

The most generally important of Thomsen's conclusions are those concerning the thermochemical phenomena of isomeric carbon compounds. With regard to his statement that the four valencies of the carbon atom have equal thermal values, it is to be remarked that this conclusion is obtained by using certain values for the heats of combustion of various hydrocarbons which differ very considerably from the values obtained by Thomsen himself at other times. Moreover, the argument involves certain unverified assumptions; for instance, that the molecule of gaseous carbon is diatomic. And, in the course of his argument, Thomsen sometimes uses the expressions *chemical value of a bond*, and *thermal value of a bond* as synonymous, and sometimes with different meanings.[1]

I have already, in this chapter, referred to Brühl's division of isomerides into the two classes of *position-isomerides*, that is, those which differ in the distribution of their interatomic reactions but not in the number of single, double, etc., linkings, and *saturation-isomerides*, that is, those which differ in the actual valencies of their atoms, in the number of single, double,

---

[1] Compare Brühl's criticism, *J prakt. Chem.* [2], **35**, 181, 209 [1887].

etc., linkings. Thomsen's generalization regarding isomerism
asserts that the heats of combustion and the heats of formation
of *saturation-isomerides* may and do differ, but that *position-
isomerides* have equal heats of combustion and of formation.

I will consider Brühl's experimental criticism of Thomsen's
conclusion, and at the same time give some account of his
thermochemical argument to prove that the benzene nucleus
contains three double linkings, and not, as Thomsen asserted,
nine single linkings.[1]

Horstmann [2] said that when CH_4 and C_3H_8 react to form
$C_4H_{10} + H_2$, the heat of combustion is decreased by 5400 cals.;
and that when C_2H_6 becomes $C_2H_4 + H_2$, the heat of combustion
is decreased by 3600 cals. From these data and other data
similar to these, Horstmann concluded that the single linking
of two carbon atoms has a constant thermal value equal to
5400 cals., and the double linking of two carbon atoms has a
constant thermal value equal to 3600 cals. Thomsen concluded
that a single linking between two carbon atoms is thermally
equal to a double linking, and that each has a value between
14,000 and 15,000 cals. From the thermal values which he
assigned severally to single and double linkings of two carbon
atoms, Horstmann endeavoured to prove that benzene has nine
single linkings. His argument ran thus. The difference between
hexane, C_6H_{14}, and benzene, C_6H_6, is eight atoms of hydrogen.
If benzene has nine single linkings, that is, four more than
hexane, the heat of combustion of benzene should be 4×5400
$= 21,600$ cals. less than that of hexane. But if benzene has
three double linkings, the heat of combustion of this hydro-
carbon should be $5400 + (3 \times 3600) = 16,200$ cals. less than that
of hexane, because three double linkings and one single linking
are formed in passing from hexane to benzene. Thomsen's data
give 19,990 cals., and Stohmann's data give 21,170 cals., as
the difference between the heats of combustion of hexane and
benzene. The mean difference (20,580 cals.) is much nearer
that calculated on the assumption of nine single linkings than
that calculated on the assumption that Kekulé's formula for

---

[1] Brühl, *J. prakt. Chem.* [2], **49**, 201 [1894]
[2] *Berichte*, **21**, 2211 [1888].

benzene is correct. Hence, Horstmann concluded that benzene has nine single linkings between its atoms of carbon.

Brühl (l.c.) attempted to prove that no constant thermal value can be given either to a single linking or to a double linking between two atoms of carbon; that position-isomerides as well as saturation-isomerides have not always the same heat of combustion. He cited many data, most of them from Stohmann's memoirs, which enabled him to compare the heats of combustion of many compounds related so that the passage from one to another consists in the loss of two atoms of hydrogen, and the formation of a single linking between two atoms of carbon, and he showed that the heats of combustion vary from 26,000 to 30,000 cals. By comparing compounds of different classes, formed one from another by the loss of two atoms of hydrogen, and the formation of a double carbon linking, Brühl showed that the differences between the heats of combustion of these compounds vary from 8600 to 50,600 cals. Reviewing these results, Brühl said:

"The constitutive character of the calorimetric constants, whereby even the simplest rules of homology are limitedi and modfied, is shown in a marked way."

And again:

"Single and double linkings often behave thermally in almost or altogether the same manner."

As Stohmann gave the same heat of combustion to the isomerides phenanthrene and anthracene, Brühl said that paralinkings may have the same thermal value as ethylenic linkings in aromatic compounds.

Brühl's general conclusion was that trustworthy conclusions regarding single or double linkings in benzene cannot be drawn from the observed differences between the heats of combustion of that hydrocarbon and hexane. But, Brühl said, Stohmann's thermal investigation of compounds produced by hydrogenizing closed rings gives data which help to solve the problem of the structure of benzene. Stohmann [1] compared the heats of combustion of hydrogenized terephthalic acids of known structure

---

[1] F. Stohmann and Langbein, *J. prakt. Chem.* [2], **48**, 447 [1893].

with the heats of combustion of hydrogenized benzenes of known structure, and showed the existence of certain marked regularities. He concluded that

"The linkings are most stable in the intact benzene nucleus; they are loosest in the di- tri- and tetra-hydrogen compounds; in the hexa-hydrogen compounds the linkings again attain a high degree of stability, which, however, is not so great as in the original nucleus."

When the thermal energy associated with a linking is less than that associated with another linking, the former linking is said to be more stable than the latter.

Stohmann also drew the conclusion that

"There cannot be three equivalent double linkings in the benzene nucleus."

Brühl said that the first of Stohmann's conclusions is an undoubted statement of facts, but the second is purely hypothetical. By making a detailed comparison of the differences between the heats of combustion of hydrogenized ring-compounds and the differences between the structural formulæ of these compounds, Brühl tried to prove that no absolute thermal value can be assigned to a double linking, that the value depends on the structure of the compounds wherein the double linking is found. Thermal values, Brühl said, are conditioned by everything that conditions the stabilities of the molecules which are considered; for instance, by the presence and the relative positions of more or less negative atomic groups in the molecules. Brühl concluded that the change from hydrogenized compounds to benzene is not accomplished by steps which are thermally regular.[1] Finally, Brühl said:

"The fundamental cause of the stability of benzene . . . is to be sought for in the symmetry of its construction. But thermodynamic investigation has been the first means to furnish the numerical data for the argument which proves this assertion."

The fact, noticed in the foregoing paragraphs, that very different conclusions regarding the meaning of thermal data bearing on the subject of isomerism have been drawn by investigators of great ability, shows how difficult it is to dissect

---

[1] Compare Brühl's conclusions regarding these processes drawn from spectrometric data, and described in this chapter, pp. 471–476.

the thermal values of chemical changes and to interpret thermochemical data.

In 1903, *a new law in thermochemistry* was announced by F. W. Clarke.[1] Clarke's generalizations are based, for the most part, on the data in the fourth volume of Thomsen's *Untersuchungen*. If the reasoning is sound, a great advance is undoubtedly made towards the simplification and the understanding of the connexions between chemical composition and thermal changes. Clarke concluded that "the absolute heat of formation of any chemical compound is a function of the number of atomic unions in the molecule"; that in certain classes of organic compounds the absolute heat of formation is directly proportional to the number of atomic unions, and in all organic compounds is a whole multiple of a single constant; and that the thermal value of an atomic union is independent of the masses of the two atoms which are united. But, when one follows Clarke's reasoning, one finds that the argument assumes the conclusion that the absolute heat of formation of a compound (that is, the heat of formation of a molecular weight of the compound from gaseous atoms of its elements) is proportional to the number of atomic linkings.

Clarke gives many examples of calculated "absolute heats of formation," but there is no method of testing experimentally the accuracy of these numbers. They are obtained by using a formula which implicitly contains what it is desired to prove. Moreover, if Clarke's method of calculation is adopted, it is necessary to asume that the thermal value of an atomic linking is always the same whether it be a single, double, or treble linking, and whatever may be the atoms which are linked. In other words, it is necessary to assume that all isomerides have the same heat of combustion. But it has been proved by many investigators that there are often great differences between the heats of combustion of isomerides. Stohmann has proved that even in cases of geometrical isomerism, the metastable form has often a greater heat of combustion than the stable form.[2]

What Clarke's treatment of thermochemical data seems

[1] *Proc. Washington Academy of Sciences*, **5**, pp. 1 to 97 [1903].
[2] *J. prakt. Chem.* [2], **48**, 447 [1893].

to me to prove is, that the heats of combustion of many carbon compounds are approximately whole multiples of a constant, which is about 13,700 cals.; provided the heats of combustion are stated for the carbon compound, and the products of combustion, in the gaseous state, at about 18°. Clarke also gives an empirical rule for finding the number whereby 13,700 must be multiplied in order to obtain the heat of combustion of any one of the compounds which he enumerates. Clarke draws attention to the fact that 13,700 cals. is the heat of neutralization of a strong acid by a strong base, that is, according to the ionic hypothesis, the heat of formation of a molecule of water from hydrion and hydroxidion.

In his *Thermochemical Investigations*, Hess claimed that his data proved the heat of neutralization of an acid to be the same whether the base was potash, soda, ammonia, or lime. He said that facts about the affinities of bases contradicted the conclusion, which seemed to follow from these data, that the affinities of the four bases for a specified acid are the same. The heat of neutralization of an acid by a base was declared by Hess to be the difference between the heats produced by the combination of the base with water and with acid respectively. He found that when lime combined with water to form the hydrate, 163 units of heat were produced, and when potash formed the hydrate, about 320 units of heat were produced. He had given the value 410 units to the heat of neutralization of nitric acid by potash or by lime. Hence, Hess concluded that the combination of potash with an acid produces more heat than is produced by the combination of lime with the same acid, and that, therefore, the affinity of potash for an acid is greater than the affinity of lime for the same acid.

The argument of Hess is perhaps clearer when it is put into the following form.

$$\text{Base} + \text{water} = x \text{ units of heat.}$$
$$\text{Base} + \text{acid} = y \text{ " " "}$$

Heat of neutralization $= y - x$ units $=$ constant, independent of the base.

For lime and nitric acid, $y - x = 410$ units. For potash and nitric acid, $y - x = 410$ units.

For lime and water, $x = 163$ units. For potash and water, $x = 320$ units.

Therefore, for lime, $y = 573$ units; and for potash, $y = 730$ units.

Therefore, the affinity of potash for nitric acid is considerably greater than the affinity of lime for the same acid.

Hess assumed the existence of a quantitative connexion between the thermal values of definite chemical processes and the affinities of the substances concerned in these processes. He expressed the hope that "the accurate measurements of quantities of heat will provide a relative measure of affinity and lead to the discovery of its laws."

Thomsen and Berthelot both spent much labour in measuring the affinities of substances by thermochemical methods.

In 1854, Thomsen supposed that the relation between affinity and thermal changes is very simple.[1] He defined *affinity* to be "the force which holds together the constituents of a compound"; and he said that "to measure affinity, to decompose a compound, a force is needed whose magnitude can be measured by the thermal value of the formation of the compound from the aforesaid constituents." By reasoning of this kind, Thomsen deduced the conclusion that

"Every simple or complex action of a purely chemical character is accompanied by production of heat."

In 1882, in which year the first and second volumes of his *Untersuchungen* were published, Thomsen recognized that the relations between affinity and thermal data are more complicated than he had supposed when he began the examination of them. He said that the occurrence of a chemical reaction, and the nature of the products, are dependent chiefly on the following four influences. The striving of the atoms towards the satisfaction of their stronger affinities, that is, towards those positions of stable equilibrium the attainment of which is accompanied by the maximum outflow of energy; the resistance of the molecules to change, resistance which favours

[1] *Pogg. Annal.*, **92**, 34 [1854].

whatever reaction is attended by the minimum outflow of energy; the temperature of the reaction; and the stability of the possible products at the temperature of the reaction.[1] Thomsen spoke of the thermochemical data which deal with these four circumstances for any class of elements or of compounds, as the affinity-phenomena of that class of substances. He was careful to notice that thermochemical data "do not give any direct information regarding the magnitude of the forces at work in chemical processes, partly because these data are merely expressions of the differences between the energies of the molecules which are decomposed and of those which are produced, and partly because they are often affected by non-chemical reactions which accompany the chemical changes." He defined *affinity* to be "the mutual action of atoms, their attractions, and their unequal capacities of combination." [2]

In the first volume of his *Untersuchungen*,[3] Thomsen gave the following modified form of his *dictum* of 1854, quoted above.

"Investigations in the domain of the mechanical theory of heat lead to the generalization that 'the entropy of the world tends to a maximum.' In agreement with this statement is the experience that the great multitude of chemical processes which are accomplished without the aid of foreign energy, and are free from by-reactions, are accompanied by production of heat."

In his *Essai de Mécanique Chimique*, published in 1879, Berthelot defined *affinity* to be "the resultant of the actions which hold together the elements of compounds."

"In studying that resultant," Berthelot said,[4] "one must take account of natural actions which may modify, that is to say, determine or facilitate either the combination of the elements or the decomposition of the compounds. Such are heat, electricity, light, or even, in some cases, the mechanical effects of shock or of pressure."

Having divided the heat disengaged in a chemical process into two parts, that developed by chemical energies and that developed by physical energies, Berthelot said that the heat has its source in re-arrangements of the chemical particles

---

[1] *Untersuchungen*, ii, pp. 460–474.
[2] *Ibid.*, i, pp. 1, 3.
[3] *Ibid.*, i, p. 12.
[4] *Mécanique Chimique*, i, p. xxiv.

gróups of which form the physical molecules of a substance, and in re-arrangements of the portions of these chemical particles.[1]

Berthelot accepted the molecular conception of the structure of elements and of compounds, but he used the molecular and atomic theory in a half-hearted manner. The result was that here, as elsewhere, a half-hearted devotion was not an acceptable service. To accept a scientific hypothesis is not to accept an infallible, unverifiable dogma. It is to make the most of an instrument for correlating known facts and suggesting lines of inquiry. If the hypothesis is worth using, its fundamental assumptions, its meaning, its limitations, and, to some extent, the scope of its application, must be understood. It is the hypothesis itself, not something that is superficially like it, which must be used. Berthelot thought in molecules; he refused to think in molecules and atoms. He preferred to think in molecules and equivalents;[2] and so he fell into that confusion from which Avogadro and Cannizzaro rescued chemists long ago.

Having given a loose definition of affinity, and a partial analysis of the sources of the heats of chemical reactions, Berthelot laid down three principles; the principle of molecular actions, the principle of the calorimetric equivalency of chemical transformations, and the principle of maximum work. The second of these is the generalization made by Hess, that the heat produced in a chemical change is always the same, whether the change proceed all at once or in any number of separate steps. I give Berthelot's other principles in a translation of his own words.[3]

"PRINCIPLE OF MOLECULAR ACTIONS.—*The quantity of heat disengaged in any reaction measures the sum of the chemical and the physical changes accomplished in that reaction.* This principle furnishes the measure of chemical affinities.

---

[1] *Mécanique Chimique*, i, p. xxvii.
[2] Berthelot uses equivalent weights, equal to half the atomic weights, of aluminium, carbon, calcium, copper, oxygen, sulphur, zinc, and many other elements. Hence many of his formulæ must be translated into ordinary chemical language before his thermochemical data are comparable with those of other investigators.
[3] *Mécanique Chimique*, i, pp. xxviii, xxix.

PRINCIPLE OF MAXIMUM WORK.—*Every chemical change accomplished with-out the intervention of external energy tends to the production of that body, or that system of bodies, which disengages most heat.*

The forecast of chemical phenomena is referred by this principle to the purely physical and mechanical conception of the maximum work accom-plished by molecular actions.

Let us notify the following announcement, which is deduced from the preceding and is applicable to a multitude of phenomena.

Every chemical change which can be accomplished without the aid of a pre-liminary action, and without the intervention of energy foreign to that of the bodies present in the system, necessarily happens if it disengages heat."

The principle of molecular actions and the principle of the calorimetric equivalency of chemical transformations are de-veloped, and experimentally illustrated, in the first volume of *Mécanique Chimique*. That volume contains an experimental investigation of the rules and the general methods of chemical calorimetry, and gives Berthelot's data concerning "the quan-tities of heat disengaged or absorbed in the various changes of state, physical or chemical, which bodies are capable of exhibit-ing in our laboratories." The second volume is devoted to the consideration of *chemical mechanics*, "that is to say, the study of the conditions which determine and regulate chemical reac-tions." That volume is divided into two parts. The first part deals with "the general study of chemical combination and de-composition; it embraces what one might perhaps call *chemical dynamics*." The second part "contains *chemical statics*, properly so called, founded on the principle of maximum work."

Berthelot's book deals with the fundamental principles of a branch of physical chemistry; it is marked by boldness of de-sign and originality of treatment. One of the important results of Berthelot's thermochemical work was the establishment of marked similarities between chemical equilibria and physical equilibria. Indeed, I think that the *Mécanique Chimique* would best be described as a thermochemical investigation of equilib-rium. The law of maximum work was stated very rigidly by Thomsen in 1854, less rigidly by him in 1882, and by Berthelot in 1879 with certain qualifying phrases which opened possible ways of escape. Although that proposition has been proved to be too loose, in that it does not define *purely chemical actions*, and too rigid, in that it asserts the necessary occurrence of a

chemical reaction if heat is disengaged thereby, nevertheless the law of maximum work, and especially the applications of it made by Berthelot, helped to elucidate some of the conditions of chemical equilibrium, and to prepare the way for the principle of mobile equilibrium. I have drawn attention (Chapter XV, pp. 438, 439) to van't Hoff's demonstration that only "at the absolute zero point do compounds formed with evolution of heat replace the others completely," and to his deduction from the principle of mobile equilibrium that "those chemical changes which occur at the ordinary temperature must, in the majority of cases, be accompanied by evolution of heat." The law of maximum work has not that universal applicability which was assigned to it by Thomsen and by Berthelot. It is not a law; but, if employed with caution and skill, it is a useful guide in making comparisons of chemical changes from considerations of the quantities of energy which change form in these processes, and in predicting possible reactions.

Hess thought that determinations of the quantities of heat produced in chemical interactions would probably lead to a measure of chemical affinity. Thomsen measured chemical affinity by determinations of the heats of chemical reactions, but he was careful to use the term *affinity* as including various actions and reactions, and to give to it a very wide and general connotation. Berthelot (*Mécanique Chimique*, i, p. 1) said: "The work of affinity is measured by the quantity of heat disengaged in chemical transformations accomplished in the act of combination."

Is the heat of a chemical reaction a measure of the affinities of the substances which take part in that reaction?

We have seen (pp. 329, 330) that in the fifties of the last century Hittorf laid the foundations of the electrochemical hypothesis that the rate of transport of electricity by the ions of an electrolyte is proportional to the rapidity of the chemical reactions which are dependent on that electrolyte, but that rates of electrical conductivity do not measure affinities of ions. This view was enforced by Helmholtz in 1881, who showed that the quantity of electricity on atoms does not increase in proportion to the affinities of the atoms (p. 335). Berzelius had regarded

increase of affinity as nearly synonymous with increase of electrical charge. He taught that each substance, each kind of atom, has a specific unipolarity; but, by recognizing differences in the intensities of polarities, he acknowledged that affinity is not measured solely by quantity of electricity. That one of several substances which has the greatest tendency to neutralize the electricity of another substance has the greatest affinity, according to Berzelius. By 'greatest tendency to neutralize electricity,' Berzelius seems to have meant 'power of neutralizing the largest quantity of electricity.' The scientific instinct of Berzelius gave him an inkling, although it did not enable him to form a clear conception of the distinction between the two factors, the quantity-factor and the intensity-factor of electrical energy.

The meaning of the Berzelian expression, *unequal intensities of polarization*, was elucidated by the electrochemical theory of Arrhenius (pp. 333, 413), that both chemical reactivity and electrical conductivity depend on the ratio of ionized to unionized molecules in the solution of an electrolyte, and therefore great tendency to ionize means large affinity; for the word *tendency* here connotes a difference in the intensity of a quantity of energy (Ostwald, *Lehrbuch*, **2** (i), p. 873). A substance the affinity of which is large, is regarded by the theory of Arrhenius to be a substance which readily ionizes, that is, has a great intensity of electrical and chemical energy. The electronic theory asserts that the chief conditions which determine readiness to ionize are the number, the motions, and the configuration of the corpuscles which form the atom, and that these conditions may be influenced, to some extent, by external circumstances (p. 348).

The connexions between the factors of electrical energy and the factors of chemical energy have been investigated, and it has been shown that differences of affinity, that is, of intensity of chemical energy, can be expressed in terms of electromotive force, that is, of intensity of electrical energy [1] (p. 429).

---

[1] The student may profitably consult Chapter III of Lehfeldt's *Electrochemistry*.

The foregoing brief retrospect shows that the conception of the difference between quantity of electricity and intensity of electricity was slowly acquired by physical chemists. Berzelius made an incomplete analysis of the concept *electricity*. Hess, Thomsen, and Berthelot made an incomplete analysis of the concept *heat*. It is necessary to distinguish between quantity of electricity and intensity (or pressure) of electricity when dealing with electrical energy; and it is necessary to distinguish quantity of heat from intensity of heat when dealing with thermal energy.

The quantity of heat disengaged in a chemical reaction measures the loss of chemical energy, and, in most cases, of certain other forms of energy suffered by the system which has changed. But chemical changes are conditioned by the quality as well as by the quantity of energy which changes its form.

If affinity were thought of as a force, the work done by affinity could be measured by the heat of a reaction at absolute zero.

"At absolute zero the heat produced in a chemical transition is a measure of the work done by the affinity, and the sign shows the direction which the transition will follow." [1]

But the temperature of chemical laboratories is not absolute zero. When one deals with a system which is characterized by having a transition-temperature, then

"The work, expressed in calories, which the affinity can accomplish at a given temperature, is equal to the quantity of heat which causes the transition divided by the absolute temperature of the transition-point and multiplied by the difference between that temperature and the temperature whereat the transition happens." [2]

It is evident, then, that the heats of chemical reactions are not measures of the affinities of the substances which take part in these reactions. For the heat of a reaction is the sum of several thermal changes, some of which are rather physical than chemical; and if determinations were made of the quantities of strictly chemical energy changed into thermal energy in chemical reac-

[1] Van't Hoff, *Studies* (translated from the German edition), p. 249.
[2] Van't Hoff, *ibid.*, pp. 247, 248.

tions, these determinations would not measure the affinities of
the reacting substances, because affinity is only one of the
factors of chemical energy, as quantity of heat is only one of the
factors of thermal energy.

When the thermal values of chemical changes are spoken of as
measures of the affinities concerned in these changes, the word
affinity is used in a wide and loose sense.   As an example of such
usage of the term I refer the reader to p. 525, where Thomsen's
fourfold division of the thermal aspects of affinity-phenomena is
described.   That analysis exhibits some of the difficulties which
are encountered in dealing with the subject of affinity.   What is
affinity?   The cause of chemical interactions.   But what is a
chemical interaction?   The description of a chemical change
as an interaction between homogeneous substances, whereby
other homogeneous substances are formed, does not carry the
analysis far enough, if it is desired to attribute the occurrence
of the change to a single cause.   The study of affinity has ad-
vanced of late years, as Guyton de Morveau said it had advanced
in his time (1786), chiefly in the direction of classifying the
results of the affinities of substances.   We are able to assign
to many compounds numerical values which quantitatively
condition the specific reactions of these substances; we are
able to translate these affinity-constants into the language of
an electrochemical theory which co-ordinates them with many
other facts and suggests lines of inquiry; we are able to cal-
culate the work done by the affinities of the parts of the com-
pounds in question in forming these compounds, in terms of
the same electrochemical theory; and we are able to go a step
farther and, by regarding affinity as the maximum quantity of
work that can be done by a chemical reaction, obtain an instru-
ment for dealing with the problems grouped together under the
general term *affinity*, "without admitting anything concerning
the nature of affinity, or of the matter wherein the affinity is
supposed to reside." [1]

---

[1] Van't Hoff, *J. phys. Chemistry*, **9**, 81 [1905].

SUMMARY AND CONCLUSION.

FIVE hundred years before Christ chemical processes were
used by artificers and chemical theories occupied the thoughts
of philosophers. Those were the days of magnificent generaliza-
tions. The study of natural events had not been portioned out
in small allotments. The thinkers were free to wander where
they chose; there were no boundary walls to scale.

In the Middle Ages freedom of inquiry was almost impossible.
Confined by the necessities of a theological system, naturalists
interpreted nature according to rules promulgated by an author-
ity outside themselves. The results of the study of material
changes were recorded in the only language which men were
allowed to speak. As that language was artificial, the study of
nature lacked reality. Nevertheless something was gained.
Forbidden and unable to roam at will, those whose instincts
forced them to examine natural events looked more closely at
what came within the range of their vision. Natural phenomena
were divided into groups: one branch of inquiry was separated
from other branches; a beginning was made in the classification
of the sciences. In gaining some freedom of inquiry, men of
science were greatly helped by the painters, the sculptors, and
the poets of the Renaissance. The artistic interpretation of
nature was allowed when the scientific interpretation of nature
was forbidden. The modern fear of beauty was unknown in
those days.

The connexions between composition and properties gradu-
ally became a definite object of investigation. The history of
the advances and the backslidings which have marked that
investigation is the history of chemical ideas.

For many centuries properties were thought of as shells

which hid the kernel, substance. The discovery that shell and kernel are one was made very gradually.

Lavoisier gave definiteness to the notion of composition, proved that change of composition is indissolubly connected with change of properties, and furnished the science of chemistry with its object and its method. He described elements as undecompounded homogeneous substances, compounds as homogeneous substances formed by the coalescence of definite quantities of determinate elements, and chemical changes as those transformations of systems of homogeneous substances wherein neither the quantity nor the quality of the elements concerned is changed. After the work of Lavoisier the objects of chemistry were seen to be these; the examination of the concept *homogeneous substance*, the elucidation of the element and the compound, and the examination of the other concept *chemical change*, the elucidation of the conditions and the mechanism of the interactions of elements and of compounds.

The addition made by Dalton to the Greek atomic theory created a magnificent instrument of research by the use of which great advances were made in the two fundamental inquiries of chemistry. The finer problems of composition were stated and partially solved by chemists who used the Daltonian theory boldly and wisely. In the fundamentally important matter of classification that theory has done splendid service to chemistry.

From the study of changes of composition and properties in particular systems of elements and compounds many chemists have tried to formulate the general laws of chemical changes, that is, expressions of those features of chemical transmutations which are common to all instances thereof. The study of chemical equivalency, of affinity, and of equilibrium has led to generalizations of very far-reaching character regarding the interactions of homogeneous substances. Some of these generalizations, especially those concerning equilibrium, are applicable to physical changes as well as to chemical transmutations; and in this department of inquiry it has been possible to make certain general statements which hold good in all cases of equilibrium, and are independent of any theory of the structure of matter.

The chemical part of a transmutation is only a portion of the total transaction. No one can define the boundaries of chemistry, physical chemistry, chemical physics, and physics. "In nature everything is distinct, yet nothing defined into absolute independent singleness." The history of chemical ideas shows that many fundamental conceptions of chemistry have been gained by using physical methods of investigation. The ideas which guide chemists when they use the molecular and atomic theory, when they apply the periodic law, when they deduce composition from crystalline form, when they use the hypothesis of ionization, when they discuss certain aspects of chemical affinity, when they connect changes of composition with changes of energy; these and many other guiding ideas are the gifts of the physicist to the chemist. The measure has been returned by the chemist 'pressed down and running over.' By the discovery of radium the chemist has called a new world into being; and, with a fine generosity, he has given it to the physicist to investigate.

The study of the connexions between composition and properties has entered a new phase. The old questions remain. The answers which have been given by the labours of countless generations of naturalists, through more than two milleniums, have not solved these problems. Physicists and chemists have joined in the quest of finding new answers to the old questions: What is a homogeneous substance? What happens when homogeneous substances interact?

INDEX.

SHORT-TITLE CATALOGUE

OF THE

PUBLICATIONS

OF

JOHN WILEY & SONS,

NEW YORK.

LONDON: CHAPMAN & HALL, LIMITED.

ARRANGED UNDER SUBJECTS.

Descriptive circulars sent on application. Books marked with an asterisk (*) are sold at *net* prices only, a double asterisk (**) books sold under the rules of the American Publishers' Association at *net* prices subject to an extra charge for postage. All books are bound in cloth unless otherwise stated.

AGRICULTURE.

Armsby's Manual of Cattle-feeding. 12mo, $1 75
Principles of Animal Nutrition.............................8vo, 4 00
Budd and Hansen's American Horticultural Manual:
Part I. Propagation, Culture, and Improvement.................12mo, 1 50
Part II. Systematic Pomology..............................12mo, 1 50
Downing's Fruits and Fruit-trees of America 8vo, 5 00
Elliott's Engineering for Land Drainage.....................12mo, 1 50
Practical Farm Drainage.............................12mo, 1 00
Graves's Forest Mensuration.............................8vo, 4 00
Green's Principles of American Forestry.......................12mo, 1 50
Grotenfelt's Principles of Modern Dairy Practice. (Woll.)...........12mo, 2 00
Kemp's Landscape Gardening.............................12mo, 2 50
Maynard's Landscape Gardening as Applied to Home Decoration. 12mo, 1 50
* McKay and Larsen's Principles and Practice of Butter-making 8vo, 1 50
Sanderson's Insects Injurious to Staple Crops.....................12mo, 1 50
Insects Injurious to Garden Crops. (In preparation.)
Insects Injuring Fruits. (In preparation.)
Stockbridge's Rocks and Soils.............................8vo, 2 50
Winton's Microscopy of Vegetable Foods.......................8vo, 7 50
Woll's Handbook for Farmers and Dairymen....................16mo, 1 50

ARCHITECTURE.

Baldwin's Steam Heating for Buildings. 12mo, 2 50
Bashore's Sanitation of a Country House.........................12mo, 1 00
Berg's Buildings and Structures of American Railroads..............4to, 5 00
Birkmire's Planning and Construction of American Theatres..........8vo, 3 00
Architectural Iron and Steel.............................8vo, 3 50
Compound Riveted Girders as Applied in Buildings................8vo, 2 00
Planning and Construction of High Office Buildings..............8vo, 3 50
Skeleton Construction in Buildings.........................8vo, 3 00
Brigg's Modern American School Buildings......................8vo, 4 00

ARMY AND NAVY.

ASSAYING.

ASTRONOMY.

BOTANY.

CHEMISTRY.

CIVIL ENGINEERING.

BRIDGES AND ROOFS.   HYDRAULICS.   MATERIALS OF ENGINEERING. RAILWAY ENGINEERING.

Taylor and Thompson's Treatise on Concrete, Plain and Reinforced....8vo, 5 00
* Trautwine's Civil Engineer's Pocket-book.............16mo, morocco, 5 00
Venable's Garbage Crematories in America......................8vo, 2 00
Wait's Engineering and Architectural Jurisprudence................8vo, 6 00
                                                            Sheep, 6 50
    Law of Operations Preliminary to Construction in Engineering and Archi-
        tecture...8vo, 5 00
                                                            Sheep, 5 50
    Law of Contracts...8vo, 3 00
Warren's Stereotomy—Problems in Stone-cutting....................8vo, 2 50
Webb's Problems in the Use and Adjustment of Engineering Instruments.
                                                    16mo, morocco, 1 25
Wilson's Topographic Surveying..............................8vo, 3 50

BRIDGES AND ROOFS.

Boller's Practical Treatise on the Construction of Iron Highway Bridges..8vo, 2 00
*   Thames River Bridge............................4to, paper, 5 00
Burr's Course on the Stresses in Bridges and Roof Trusses, Arched Ribs, and
        Suspension Bridges....................................8vo, 3 50
Burr and Falk's Influence Lines for Bridge and Roof Computations......8vo, 3 00
    Design and Construction of Metallic Bridges 8vo, 5 00
Du Bois's Mechanics of Engineering. Vol. II......................Small 4to, 10 00
Foster's Treatise on Wooden Trestle Bridges........................4to, 5 00
Fowler's Ordinary Foundations.....................................8vo, 3 50
Greene's Roof Trusses..8vo, 1 25
    Bridge Trusses...8vo, 2 50
    Arches in Wood, Iron, and Stone.............................8vo, 2 50
Howe's Treatise on Arches...8vo, 4 00
    Design of Simple Roof-trusses in Wood and Steel................8vo, 2 00
    Symmetrical Masonry Arches..................................8vo, 2 50
Johnson, Bryan, and Turneaure's Theory and Practice in the Designing of
        Modern Framed Structures.........................Small 4to, 10 00
Merriman and Jacoby's Text-book on Roofs and Bridges:
    Part I.   Stresses in Simple Trusses...........................8vo, 2 50
    Part II. Graphic Statics...................................8vo, 2 50
    Part III. Bridge Design.....................................8vo, 2 50
    Part IV. Higher Structures.................................8vo, 2 50
Morison's Memphis Bridge...4to, 10 00
Waddell's De Pontibus, a Pocket-book for Bridge Engineers..16mo, morocco, 2 00
    * Specifications for Steel Bridges...........................12mo, 50
Wright's Designing of Draw-spans. Two parts in one volume.........8vo, 3 50

HYDRAULICS.

Barnes's Ice Formation..8vo, 3 00
Bazin's Experiments upon the Contraction of the Liquid Vein Issuing from
        an Orifice. (Trautwine.)...............................8vo, 2 00
Bovey's Treatise on Hydraulics..................................8vo, 5 00
Church's Mechanics of Engineering...............................8vo, 6 00
    Diagrams of Mean Velocity of Water in Open Channels.........paper, 1 50
    Hydraulic Motors...8vo, 2 00
Coffin's Graphical Solution of Hydraulic Problems.........16mo, morocco, 2 50
Flather's Dynamometers, and the Measurement of Power............12mo, 3 00
Folwell's Water-supply Engineering.............................8vo, 4 00
Frizell's Water-power..8vo, 5 00

MATERIALS OF ENGINEERING.

9

Coolidge and Freeman's Elements of General Drafting for Mechanical Engineers..Oblong 4to, 2 50
Durley's Kinematics of Machines................................8vo, 4 00
Emch's Introduction to Projective Geometry and its Applications........8vo, 2 50
Hill's Text-book on Shades and Shadows, and Perspective. 8vo, 2 00
Jamison's Elements of Mechanical Drawing..................?........8vo, 2 50
    Advanced Mechanical Drawing..................................8vo, 2 00
Jones's Machine Design:
    Part I. Kinematics of Machinery................................8vo, 1 50
    Part II. Form, Strength, and Proportions of Parts.. ....8vo, 3 00
MacCord's Elements of Descriptive Geometry........................8vo, 3 00
    Kinematics; or, Practical Mechanism..........................8vo, 5 00
    Mechanical Drawing...4to, 4 00
    Velocity Diagrams.......................... ....8vo, 1 50
MacLeod's Descriptive Geometry.. ....Small 8vo, 1 50
* Mahan's Descriptive Geometry and Stone-cutting....................8vo, 1 50
    Industrial Drawing. (Thompson.).............................8vo, 3 50
Moyer's Descriptive Geometry.....................................8vo, 2 00
Reed's Topographical Drawing and Sketching.......................4to, 5 00
Reid's Course in Mechanical Drawing...............................8vo, 2 00
    Text-book of Mechanical Drawing and Elementary Machine Design.8vo, 3 00
Robinson's Principles of Mechanism................................8vo, 3 00
Schwamb and Merrill's Elements of Mechanism.....................8vo, 3 00
Smith's (R. S.) Manual of Topographical Drawing. (McMillan.) 8vo, 2 50
Smith (A. W.) and Marx's Machine Design...........................8vo, 3 00
* Titsworth's Elements of Mechanical Drawing...............Oblong 8vo, 1 25
Warren's Elements of Plane and Solid Free-hand Geometrical Drawing.12mo, 1 00
    Drafting Instruments and Operations..........................12mo, 1 25
    Manual of Elementary Projection Drawing.....................12mo, 1 50
    Manual of Elementary Problems in the Linear Perspective of Form and
        Shadow...12mo, 1 00
    Plane Problems in Elementary Geometry.......................12mo, 1 25
    Primary Geometry..12mo, 75
    Elements of Descriptive Geometry, Shadows, and Perspective.......8vo, 3 50
    General Problems of Shades and Shadows 8vo, 3 00
    Elements of Machine Construction and Drawing.................8vo, 7 50
    Problems, Theorems, and Examples in Descriptive Geometry.......8vo, 2 50
Weisbach's Kinematics and Power of Transmission. (Hermann and
        Klein.)...8vo, 5 00
Whelpley's Practical Instruction in the Art of Letter Engraving. 12mo, 2 00
Wilson's (H. M.) Topographic Surveying............................8vo, 3 50
Wilson's (V. T.) Free-hand Perspective.............................8vo, 2 50
Wilson's (V. T.) Free-hand Lettering... ....8vo, 1 00
Woolf's Elementary Course in Descriptive Geometry.............Large 8vo, 3 00

ELECTRICITY AND PHYSICS.

Anthony and Brackett's Text-book of Physics. (Magie.).........Small 8vo, 3 00
Anthony's Lecture-notes on the Theory of Electrical Measurements....12mo, 1 00
Benjamin's History of Electricity..................................8vo, 3 00
    Voltaic Cell. .:...8vo, 3 00
Classen's Quantitative Chemical Analysis by Electrolysis. (Boltwood.).8vo, 3 00
* Collins's Manual of Wireless Telegraphy.........................12mo, 1 50
                                       Morocco, 2 00
Crehore and Squier's Polarizing Photo-chronograph. 8vo, 3 00
Dawson's "Engineering" and Electric Traction Pocket-book.16mo, morocco, 5 00
10

LAW.

MANUFACTURES.

MATHEMATICS.

12

Mathematical Monographs. Edited by Mansfield Merriman and Robert
  S. Woodward. . . . . .Octavo, each 1 00
    No. 1. History of Modern Mathematics, by David Eugene Smith.
    No. 2. Synthetic Projective Geometry, by George Bruce Halsted.
    No. 3. Determinants, by Laenas Gifford Weld. No. 4. Hyper-
    bolic Functions, by James McMahon. No. 5. Harmonic Func-
    tions, by William E. Byerly. No. 6. Grassmann's Space Analysis,
    by Edward W. Hyde. No. 7. Probability and Theory of Errors,
    by Robert S. Woodward. No. 8. Vector Analysis and Quaternions,
    by Alexander Macfarlane. No. 9. Differential Equations, by
    William Woolsey Johnson. No. 10. The Solution of Equations,
    by Mansfield Merriman. No. 11. Functions of a Complex Variable,
    by Thomas S. Fiske.
Maurer's Technical Mechanics. 8vo, 4 00
Merriman's Method of Least Squares. 8vo, 2 00
Rice and Johnson's Elementary Treatise on the Differential Calculus. .Sm. 8vo, 3 00
    Differential and Integral Calculus. 2 vols. in one. . . . . .Small 8vo, 2 50
Wood's Elements of Co-ordinate Geometry. 8vo, 2 00
    Trigonometry: Analytical, Plane, and Spherical 12mo, 1 00

MECHANICAL ENGINEERING.

MATERIALS OF ENGINEERING, STEAM-ENGINES AND BOILERS.

Bacon's Forge Practice. 12mo, 1 50
Baldwin's Steam Heating for Buildings. 12mo, 2 50
Barr's Kinematics of Machinery. 8vo, 2 50
* Bartlett's Mechanical Drawing. 8vo, 3 00
* "   "   "   Abridged Ed. 8vo, 1 50
Benjamin's Wrinkles and Recipes. 12mo, 2 00
Carpenter's Experimental Engineering. 8vo, 6 00
    Heating and Ventilating Buildings. 8vo, 4 00
Cary's Smoke Suppression in Plants using Bituminous Coal. (In Prepara-
    tion.)
Clerk's Gas and Oil Engine. . . . . .Small 8vo, 4 00
Coolidge's Manual of Drawing. . . . . .8vo, paper, 1 00
Coolidge and Freeman's Elements of General Drafting for Mechanical En-
    gineers. . . . . .Oblong 4to, 2 50
Cromwell's Treatise on Toothed Gearing. 12mo, 1 50
    Treatise on Belts and Pulleys. 12mo, 1 50
Durley's Kinematics of Machines. 8vo, 4 00
Flather's Dynamometers and the Measurement of Power. 12mo, 3 00
    Rope Driving. 12mo, 2 00
Gill's Gas and Fuel Analysis for Engineers. 12mo, 1 25
Hall's Car Lubrication. 12mo, 1 00
Hering's Ready Reference Tables (Conversion Factors). . . . . .16mo, morocco, 2 50
Hutton's The Gas Engine. 8vo, 5 00
Jamison's Mechanical Drawing. 8vo, 2 50
Jones's Machine Design:
    Part I. Kinematics of Machinery. 8vo, 1 50
    Part II. Form, Strength, and Proportions of Parts. 8vo, 3 00
Kent's Mechanical Engineers' Pocket-book. . . . . .16mo, morocco, 5 00
Kerr's Power and Power Transmission. 8vo, 2 00
Leonard's Machine Shop, Tools, and Methods. 8vo, 4 00
* Lorenz's Modern Refrigerating Machinery. (Pope, Haven, and Dean.) . .8vo, 4 00
MacCord's Kinematics; or Practical Mechanism. 8vo, 5 00
    Mechanical Drawing. 4to, 4 00
    Velocity Diagrams. 8vo, 1 50

MacFarland's Standard Reduction Factors for Gases. 8vo, 1 50
Mahan's Industrial Drawing. (Thompson.). .8vo, 3 50
Poole's Calorific Power of Fuels. 8vo, 3 00
Reid's Course in Mechanical Drawing. 8vo, 2 00
    Text-book of Mechanical Drawing and Elementary Machine Design.8vo, 3 00
Richard's Compressed Air 12mo, 1 50
Robinson's Principles of Mechanism. 8vo, 3 00
Schwamb and Merrill's Elements of Mechanism. 8vo, 3 00
Smith's (O.) Press-working of Metals. 8vo, 3 00
Smith (A. W.) and Marx's Machine Design. 8vo, 3 00
Thurston's Treatise on Friction and Lost Work in Machinery and Mill
    Work. 8vo, 3 00
    Animal as a Machine and Prime Motor, and the Laws of Energetics.12mo, 1 00
Warren's Elements of Machine Construction and Drawing. 8vo, 7 50
Weisbach's Kinematics and the Power of Transmission. (Herrmann—
    Klein.). 8vo, 5 00
    Machinery of Transmission and Governors. (Herrmann—Klein.). .8vo, 5 00
Wolff's Windmill as a Prime Mover. 8vo, 3 00
Wood's Turbines. 8vo, 2 50

MATERIALS OF ENGINEERING.

* Bovey's Strength of Materials and Theory of Structures. 8vo, 7 50
Burr's Elasticity and Resistance of the Materials of Engineering. 6th Edition.
    Reset. 8vo, 7 50
Church's Mechanics of Engineering. 8vo, 6 00
* Greene's Structural Mechanics 8vo, 2 50
Johnson's Materials of Construction. 8vo, 6 00
Keep's Cast Iron. 8vo, 2 50
Lanza's Applied Mechanics. 8vo, 7 50
Martens's Handbook on Testing Materials. (Henning.) 8vo, 7 50
Maurer's Technical Mechanics. 8vo, 4 00
Merriman's Mechanics of Materials. 8vo, 5 00
    Strength of Materials. 12mo, 1 00
Metcalf's Steel. A manual for Steel-users. 12mo, 2 00
Sabin's Industrial and Artistic Technology of Paints and Varnish. 8vo, 3 00
Smith's Materials of Machines. 12mo, 1 00
Thurston's Materials of Engineering. . . . . .3 vols., 8vo, 8 00
    Part II. Iron and Steel. 8vo, 3 50
    Part III. A Treatise on Brasses, Bronzes, and Other Alloys and their
        Constituents. 8vo, 2 50
Text-book of the Materials of Construction. 8vo, 5 00
Wood's (De V.) Treatise on the Resistance of Materials and an Appendix on
    the Preservation of Timber. 8vo, 2 00
    Elements of Analytical Mechanics. 8vo, 3 00
Wood's (M. P.) Rustless Coatings: Corrosion and Electrolysis of Iron and
    Steel. 8vo, 4 00

STEAM-ENGINES AND BOILERS.

Berry's Temperature-entropy Diagram. 12mo, 1 25
Carnot's Reflections on the Motive Power of Heat. (Thurston.). 12mo, 1 50
Dawson's "Engineering" and Electric Traction Pocket-book. . . .16mo mor., 5 00
Ford's Boiler Making for Boiler Makers. 18mo, 1 00
Goss's Locomotive Sparks. 8vo, 2 00
Hemenway's Indicator Practice and Steam-engine Economy. 12mo, 2 00

MECHANICS AND MACHINERY.

●

MINERALOGY.

MINING.

17

O'Driscoll's Notes on the Treatment of Gold Ores. 8vo, 2 00
Robine and Lenglen's Cyanide Industry.   (Le Clerc.). 8vo, 4 00
* Walke's Lectures on Explosives. 8vo, 4 00
Weaver's Military Explosives. 8vo, 3 00
Wilson's Cyanide Processes. 12mo, 1 50
         Chlorination Process. 12mo, 1 50
         Hydraulic and Placer Mining. 12mo, 2 00
         Treatise on Practical and Theoretical Mine Ventilation. 12mo, 1 25

SANITARY SCIENCE.

Bashore's Sanitation of a Country House. 12mo, 1 00
*   Outlines of Practical Sanitation. 12mo, 1 25
Folwell's Sewerage.   (Designing, Construction, and Maintenance.). 8vo, 3 00
         Water-supply Engineering. 8vo, 4 00
Fowler's Sewage Works Analyses. 12mo, 2 00
Fuertes's Water and Public Health. 12mo, 1 50
         Water-filtration Works. 12mo, 2 50
Gerhard's Guide to Sanitary House-inspection 16mo, 1 00
Goodrich's Economic Disposal of Town's Refuse. . . . . .Demy 8vo, 3 50
Hazen's Filtration of Public Water-supplies. 8vo, 3 00
Leach's The Inspection and Analysis of Food with Special Reference to State
         Control. 8vo, 7 50
Mason's Water-supply. (Considered principally from a Sanitary Standpoint) 8vo, 4 00
         Examination of Water.   (Chemical and Bacteriological.). 12mo, 1 25
Ogden's Sewer Design. 12mo, 2 00
Prescott and Winslow's Elements of Water Bacteriology, with Special Refer-
         ence to Sanitary Water Analysis. 12mo, 1 25
* Price's Handbook on Sanitation. 12mo, 1 50
Richards's Cost of Food.   A Study in Dietaries. .12mo, 1 00
         Cost of Living as Modified by Sanitary Science. 12mo, 1 00
         Cost of Shelter 12mo, 1 00
Richards and Woodman's Air, Water, and Food from a Sanitary Stand-
         point. 8vo, 2 00
* Richards and Williams's The Dietary Computer. 8vo, 1 50
Rideal's Sewage and Bacterial Purification of Sewage. 8vo, 3 50
Turneaure and Russell's Public Water-supplies. 8vo, 5 00
Von Behring's Suppression of Tuberculosis. (Bolduan.). 12mo, 1 00
Whipple's Microscopy of Drinking-water. 8vo, 3 50
Winton's Microscopy of Vegetable Foods. 8vo, 7 50
Woodhull's Notes on Military Hygiene. 16mo, 1 50
*   Personal Hygiene. 12mo, 1 00

MISCELLANEOUS.

De Fursac's Manual of Psychiatry.   (Rosanoff and Collins.). . . .Large 12mo, 2 50
Ehrlich's Collected Studies on Immunity (Bolduan). 8vo, 6 00
Emmons's Geological Guide-book of the Rocky Mountain Excursion of the
         International Congress of Geologists. . . . . .Large 8vo, 1 50
Ferrel's Popular Treatise on the Winds. 8vo, 4 00
Haines's American Railway Management. 12mo, 2 50
Mott's Fallacy of the Present Theory of Sound .16mo, 1 00
Ricketts's History of Rensselaer Polytechnic Institute, 1824–1894. .Small 8vo, 3 00
Rostoski's Serum Diagnosis. (Bolduan.). 12mo, 1 00
Rotherham's Emphasized New Testament. . . . . .Large 8vo, 2 00

Steel's Treatise on the Diseases of the Dog...........................8vo, 3 50
The World's Columbian Exposition of 1893 ....4to, 1 00
Von Behring's Suppression of Tuberculosis. (Bolduan.). 12mo, 1 00
Winslow's Elements of Applied Microscopy.........................12mo, 1 50
Worcester and Atkinson. Small Hospitals, Establishment and Maintenance;
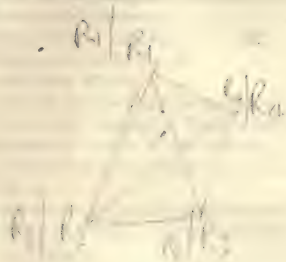   Suggestions for Hospital Architecture : Plans for Small Hospital. 12mo, 1 25

HEBREW AND CHALDEE TEXT-BOOKS.

Green's Elementary Hebrew Grammar.............................12mo, 1 25
    Hebrew Chrestomathy. 8vo, 2 00
Gesenius's Hebrew and Chaldee Lexicon to the Old Testament Scriptures.
    (Tregelles.)..........................Small 4to, half morocco, 5 00
Letteris's Hebrew Bible. 8vo, 2 25